LAPPEENRANTA UNIVERSITY OF TECHNOLOGY

Faculty of Technology

Master’s Degree Programme in Chemical and Process Engineering

Egor Gordyushenkov

UTILIZATION OF NON FERROUS METALS IN BOILER COMBUSTION ENVIRONMENT

Examiners:	Professor	Heli Siren
	Professor	Esa Vakkilainen
Supervisor	Research and Development Engineer	Irina Hyytiäinen

ABSTRACT

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Utilization of non ferrous metals in boiler combustion environment

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Keywords: non ferrous metals, chlorine induced corrosion, simultaneous thermal analysis, fluidized bed boiler.

The made research is focused on possibility of application of non ferrous metals in boiler pressure parts as a substitute of currently used ferrous-base alloys. The main issue was to define resistive ability of some perspective non ferrous metals to chlorine induced corrosion. Experimental study was performed using simultaneous thermal analysis (STA) in the temperature range of 400-700 °C. The chloride induced corrosion was simulated by mixtures of metal samples with potassium chloride treated by synthetic air. The advantage of synergetic effect of non ferrous alloys compare to single metals is shown due to the obtained data from conducted thermal balance tests.

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CONTENT

1. INTRODUCTION

Metso Power OY is the world known company (international) with the great history. It is known by its professional services and manufacturing of outstanding fluidized bed and recovery boilers. The worldwide tendency is to generate heat and power using biomass the fluidized bed boilers are used. Out of the range fluidized bed boilers *Metso Power OY* tenders bubbling fluidized bed boilers named HYBEX and circulating fluidized bed boilers – CYMIC which are briefly described in these thesis.

Study of the boiler environment is the important part of boiler design, which covers chemical and physical processes that take place inside the equipment. The type of fuel directly coupled with quality is one of the most crucial factors which should be taken into consideration. Thus, the combustion of biomass provides high temperature off gas combined with extremely corrosive content of chlorides, alkali and heavy metals.

Additionally, the mechanism of chlorine induced corrosion known as hot corrosion is under the big concern. Moreover, principals of the corrosion of non ferrous metals draw the explanation of material selection for boiler pressure parts. This study gives the general idea about the resistant behavior of different metals under highly corrosive chlorine conditions.

Summarizing, biomass utilization sets new challenges for the materials applied in boiler pressure parts. Moreover, aggressive obtained boiler environment promotes searching for new reliable materials with the possibly lowest price to lifetime ratio. Non-ferrous metals are in the most concern as a substitute for currently used ferrous materials - steels. The main reason to use the non-ferrous based materials is that they could achieve outstanding properties compare to already exploited ferrous alloys.

Finally, simultaneous thermal analysis (STA) is a well-known way to study oxidation of metals under set temperature range with simulated peculiar conditions. Difference in mass and magnitude of heat fluxes during tests give possibility to evaluate oxidation rate of the studied samples. Furthermore, this data draws a conclusion about possible utilization of the chosen material in specified conditions.

2. FLUDIZED BED BOILERS

2.1. Principles of fluidized bed combustion

The technology of fluidized bed had been used in many industrial applications since 1920's. Such processes as energy conversion, petro-chemical processing, mineral processing, chemical and pharmaceutical, physical processing were used fluidized bed due to specifically high heat and mass transfer. Since the 1970's the fluidized bed (FB) finally has found application in the energy production. The interest provided by fluidized bed technology especially in energy generation is drawn by high overall efficiency of the system, fuel flexibility – possibility to combust fossil fuel or biomass and their mixtures and low emissions of nitrogen oxides (NO_x) and sulfur dioxide (SO_2) [1, 5, 6, 8].

The general principle of fluidized bed combustion (FBC) – the fuel is burned inside a suspended layer of particles called bed. Fluidization appears when stationary layer of particles such as, sand, limestone, coal ash etc. is treated by uniform air/gas flow. Thus, the introduced flux passes through the bed starting from the bottom and compensates the gravity force. In the beginning particles remain stagnant because (Figure 2.1 a), but further increase in air/gas velocity gives fluidization – the solid layer of particles behaves as a liquid (Figure 2.1 b-d). As a result of fluidization the volume of the bed increases due to higher content of air/gas in initial voids [1, 5, 15].

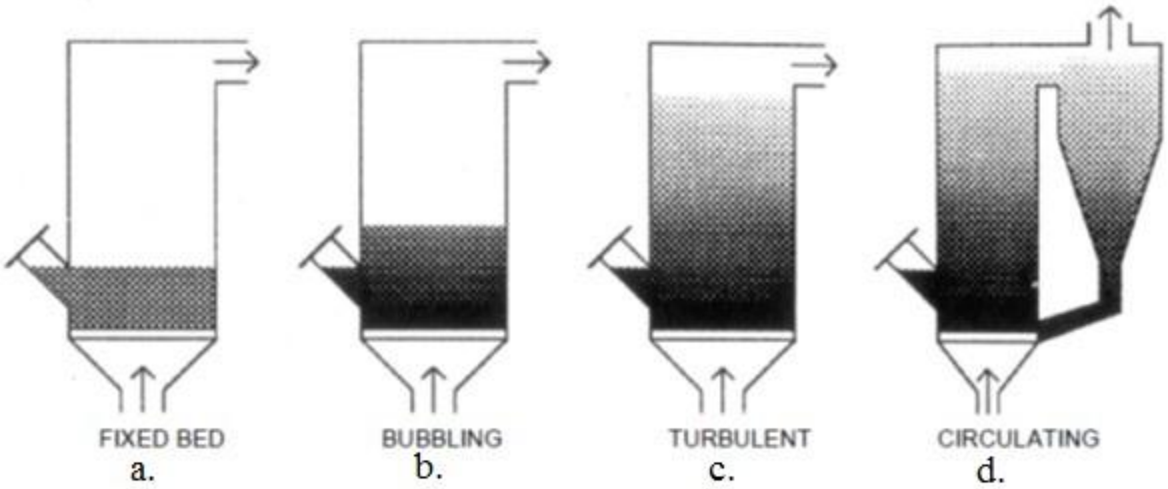

Figure 2.1. Regimes of fluidized bed systems [8].

The fluidization starts from the formation of bubbles providing rapid mixing and reduction in bed uniformity. Thus, the bed of solid particles shows the properties of a boiling liquid and is known as bubbling fluidized bed (Figure 2.1 b). The bubbling regime is known by formation of distinct boundary of the bed surface. At higher air/gas velocities bubbles start to collide with each other providing turbulent bed regime (Figure 2.1 c). Turbulent bed is the opposite of bubbling bed – particles exist inside the bed as clusters of solids. Nevertheless, turbulent regime still has a detectible bed limit and differs from bubbling mode by lower density. However, further flux increase causes entraining of particles by off gas. Therefore, a part of the solid particles have to be caught, separated from the gas and returned back to the bed in order to maintain the stability of the system. This type of the regime involving back loop of particles is known as circulating fluidized bed (Figure 2.1 d) [1, 5, 15].

The combustion of fluidized bed undergoes at about 800 to 900 °C, the temperature depends on type and chemical composition of the fuel. Another advantage of the FB combustion is a quick response to changing environment of the furnace coupled with difference in composition in the fed fuel. Operating at such temperatures below the ash fusion point allows eliminating of slagging inside the furnace, ash melting and associated problems. To maintain temperature inside the mentioned range the bed-immersed tubes are used, which absorb extra heat from combustion zone. Additionally, use of the low combustion temperature and additions of limestone or dolomite inside the fluidized bed boiler provide decrease of the nitrogen oxide (NO_x) emissions and formation of the sulfur dioxide (SO_2) [1, 3-8, 41].

2.2. Bubbling fluidized bed boiler

Generally, FB boilers could be divided on two classes depending on used type of the bed fluidization: bubbling fluidized bed (BFB) and circulating fluidized bed (CFB) [1, 5]. The bubbling fluidised bed technology was originally introduced in the late 1960’s and now it is popular tool in many industrial and combustion processes. The first applications in Finland were made for the peat combustion in municipal boilers and combustion of the bark in industrial applications. Later on the BFB technology became the cutting edge technology for combustion of biomass fuels [7].

The main parts of the boiler are fuel feed system, air distribution system and heat exchange system including furnace, superheater, economizer, air heater. The design of the typical BFB boiler is shown in Figure 2.3. The fuel feed system in bubbling bed could be divided in two types: over-bed and under-bed. The solid fuel (e.g. coal, coke) feed systems differ from the biomass systems due to excessive tendency of biomass to plug the feeding system. Thus, the common solutions for biomass are represented by techniques assisting fuel to leave the stock e.g. screw conveyor, pneumatic injector, etc. [1, 5, 9].

Primary combustion air supplied to the system is preheated in air heater. Further, the preheated air is blown inside the furnace via distribution system in order to obtain the uniformity across the bed. Distribution system of combustion air used in BFB boiler usually is two staged. In addition, the secondary injection of combustion air is used in the freeboard zone. The purpose of additional air distribution system is providing of the complete combustion of the fuel [1, 5].

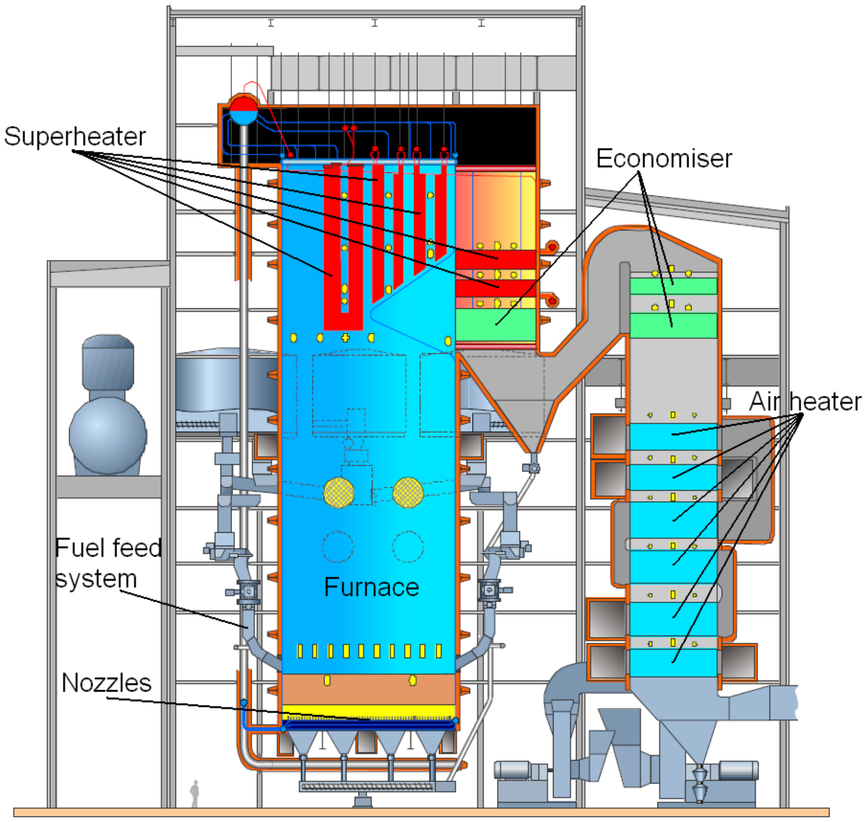

Figure 2.3. Bubbling fluidized bed boiler structure [2].

In BFB boilers, the combustion system is two-staged. While solid fuel particles burn within the bed, volatiles and very fine fuel particles are burned in the freeboard area. The freeboard area is also has a secondary air injection, in order to optimize burning. Combustion air is supplied to the bed through air pipes and bubble caps. A bubble cap is a vertical pipe with a distributor cap (Figure 2.4). The furnace of a BFB boiler, operated under atmospheric pressure, is known as atmospheric fluidized bed combustion (AFBC). When combustion is preceded at higher pressures then the BFB boiler uses pressurized fluidized bed combustion (PFBC) [1, 5].

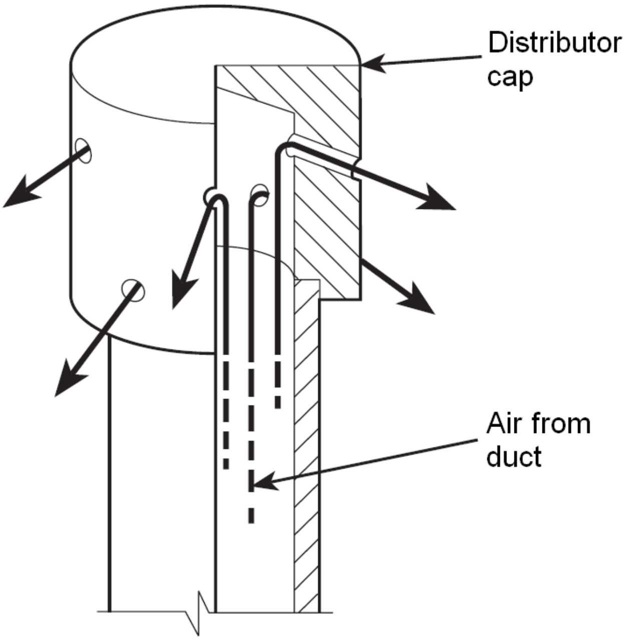

Figure 2.4. Construction of bubble cap [5].

The final BFB boiler system is the heat exchangers providing the steam generation. It is a complicated system designed in order to obtain the highest generation efficiency of the boiler. However, the heat exchange system of bubbling fluidized bed boiler is described in section *2.4. Heat exchangers in boiler environment* [1, 5, 8].

2.3. Circulating fluidized bed boiler

Application of fluidized bed combustion technology has found application in another popular type of boilers called circulating fluidized bed boilers. Despite entering the market in 1980s, they are very common in electrical power generation due to high efficiency operation and low influence to the environment. All advantages of the CFB combustion are caused by high turbulence of the operating flow that induces high mixing rate and homogenization of the temperature in the furnace [1, 5].

Operation of CFB boiler differs from BFB boiler by behavior of solid particles. Velocity of gas flow exceeds the average terminal velocity of the particles. Thus, the large fraction of solids is carried out of the bed. However, entrained particles have to be caught and then recirculated back to the furnace bed and. Thus, the occurred circulation system of the solids provides known circulating fluidized bed combustion [1, 5].

The CFB boiler design consists of the major parts, shown in Figure 2.5. The structure of the CFB boiler comprises of: fuel feed system, air distributor and nozzles, CFB loop and back pass section. The back pass section is represented by heat transfer surfaces performed as superheater, reheater, economizer and air heater. Besides, like in case of the subchapter regarding BFB boiler, peculiar description is not represented in this section. However, description of heat transfer equipment is given below in subchapter *2.4. Heat exchangers in boiler environment* [1, 3, 5, 8, 10].

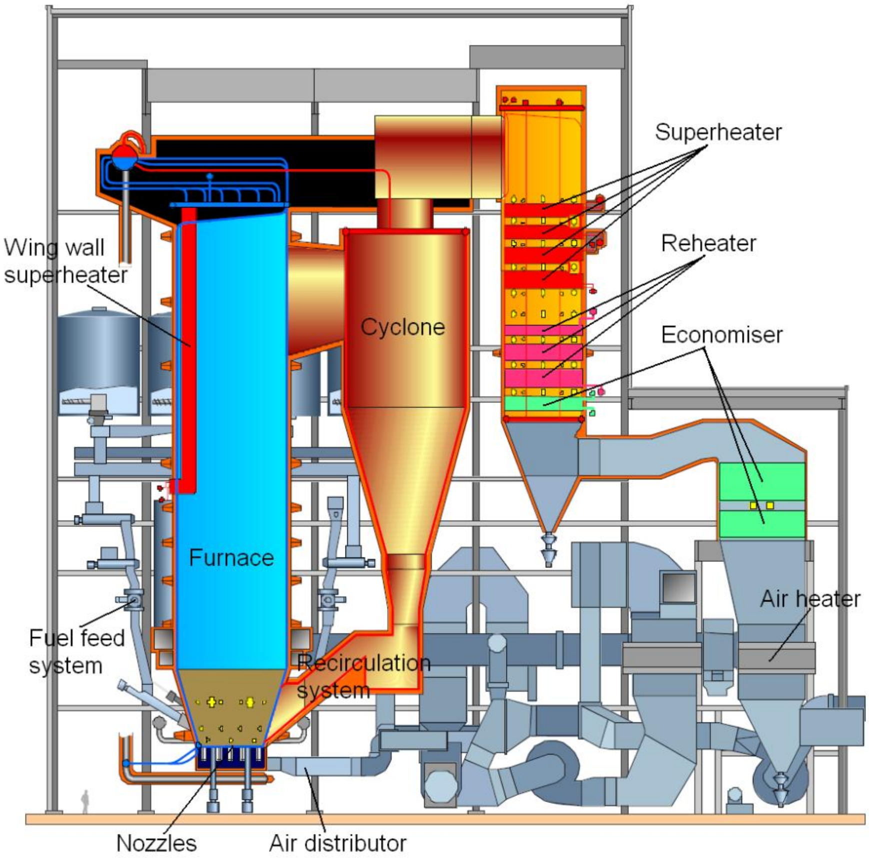

Figure 2.5. Circulating fluidized bed boiler structure [2].

Fuel is fed directly into the combustor by gravity or mechanical system. Usually the fuel is controllably fed to the combustion system by measured portions. Feeders could be installed in such a way to inject the fuel into the loop seal or to the bottom part of the furnace. In the same time feeders could be performed as a conveyors or chutes. Regarding to higher turbulence values of the flow the number of feed points in the CFB boiler is less comparing to the BFB boiler. Finally, hot fluidized bed particles heat the fuel up to the ignition temperature and cause combustion [1, 5].

The air distribution system comprises primary air fan, secondary air fan and loop seal air fan. The primary air is blown already preheated under high pressure (10-20 kPa) using the air distributor directly to the bottom of the furnace. The secondary air is supplied being preheated to the upper zone of the furnace under low pressure (5-15 kPa) in order to provide complete burning of the fuel. Additionally, the secondary air injection could be placed near the fuel feeder in order to provide entrainment of the fuel particles into the combustion flow. Finally, loop seal air fan injects air at higher pressures inside the loop seal, but without preliminary preheating [1].

The CFB loop being the main part of the boiler is represented by furnace, solid particles separator and recirculation system. The CFB loop is the heart of the CFB boiler which provides recirculating of the particles. Separation of solids undergoes in cyclones or by installation of U-beams. In the one hand the cyclone uses the radial forces to separate coarse particles out the air flow. In the other hand U-beams have U-shaped profile where coarse particle collide with the surface of beams and drop back to the furnace. Recirculation system represented by the loop seal is performed as sloped tube or conveyor connected to the lower bed [1, 5].

2.4. Heat exchangers in boiler environment

The main elements of a boiler are the heat transfer surfaces, which exchange the heat between flue gases and water/steam cycle. Heat transfer surfaces in modern boilers are: furnace/evaporator, superheater, reheater, economizer and air preheater. These surfaces cover the interior of the boiler from the furnace to the flue gas outlet [1, 5, 8, 15].

There are three different ways to transfer heat from the burning fuel to the water-steam circuit. The first is radiation which is the main mean of heat transfer in the furnace exposed to the heat released during combustion of the fuel. The second mean of heat transfer is convection coupled with radiation which is specific for superheaters and reheaters. The third and the last is convectional heat transfer predominating in air preheaters and economizers placed at the end of back pass of the flue gases [1, 5, 8].

Figure 2.3 and 2.5 give examples of the physical arrangement of heat transfer surfaces in a boiler. Moving through the flue gas path the heating surfaces are found in the sequence shown in Figure 2.3 and 2.5: furnace, superheater, reheater, economizer and air preheater. Table 2.1 presents an example of streams temperatures in heat exchanger surfaces of a boiler with steam pressure is about 80-90 bar.

Table 2.1. Typical temperatures of surfaces in heat exchangers of a boiler [8].

Boiler surface	Working fluid temperature, °C	Flue gas temperature drop, °C
Furnace/Evaporator	290-300	1400-1000
Superheaters	300-600	1000-600
Economizer	105-240	600-300
Air preheater	20-200	300-150

2.4.1. Evaporator

The evaporator is a heat exchanger which provides boiling of the water inside water circuit of the boiler. The boiling is performed by adsorbing heat released from combustion of the fed fuel. That is why the furnace, roof and flue gas channel of the boiler are parts of the evaporator. The evaporator is performed as so called membrane walls, which made of the welded tubes (Figure 2.6). Moreover, tubes are separated by flat pieces of material named membranes. Such structure is used in order to increase efficiency of radiation heat adsorption of the tubes [1, 5].

Figure 2.6. Structure of membrane tube wall [5].

2.4.2. Superheater and reheater

The main purpose of superheater is overheating the saturated steam in order to increase the efficiency (total heat adsorption) of the power production. In the same time, reheater is a superheater used for reheating the steam coming from high-pressure stage of turbine generator. Nevertheless, generally the both of them are conventional boiler heat exchangers, but operating at higher temperatures (see Table 2.1). Additionally, the superheater system is consisted of tube installations forming sophisticated water circuit (Figure 2.7.) [5, 8].

Figure 2.7. Auxiliary superheater components [5].

There are two main types of the superheaters depending on the way of heat adsorption: radiant and convection. Radiant superheaters use heat gained by radiation. That is why they placed in parts of the boiler within reach of flame radiation: walls, roof of the boiler. Convection superheaters use heat from the flue gases transferred by convection. They are situated after the boiler furnace and freeboard in zones without access of the flame radiation. Additionally, superheaters can be divided in different types due to the structure and location such as wing wall, panels and back-pass superheaters. The places of attachment of different superheater types are schematically shown in Figure 2.8 [5, 8].

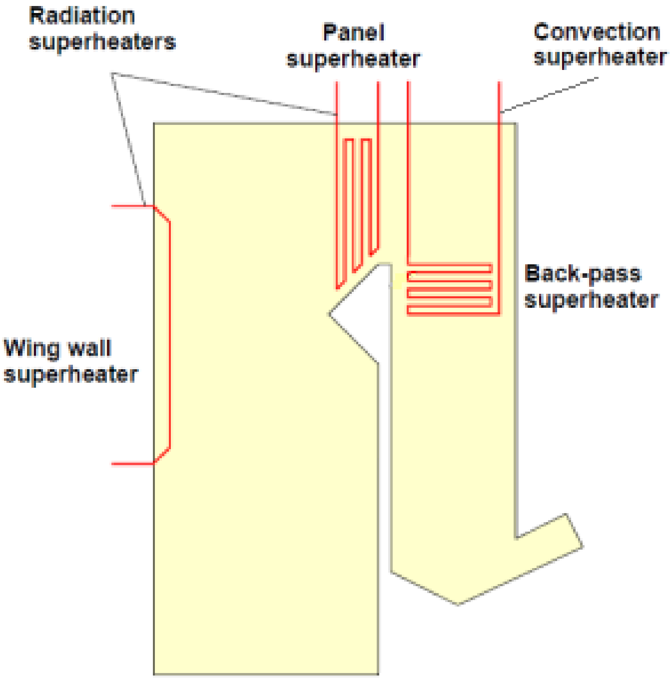

Figure 2.8. Arrangement of different types of superheaters [8].

2.4.3. Economizer

The economizer is a heat exchanger with the form of straight vertically bounded tube packages (Figure 2.9). The main purpose of the economizer is to increase the efficiency of the heat generation. Thus it raises the efficiency by cooling the flue gases leaving the superheater zone by water, which is further fed to evaporator. [5, 8].

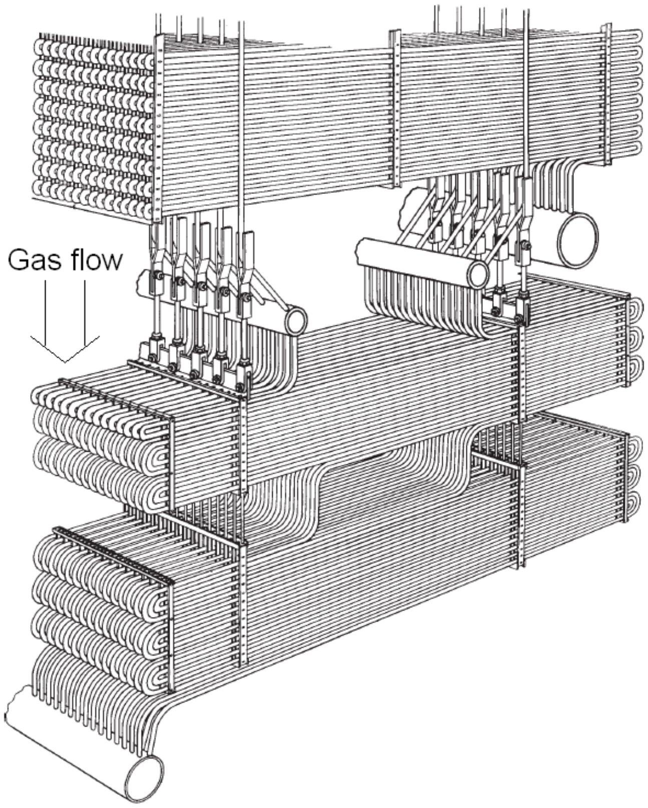

Figure 2.9. The structure of economizer [5].

2.4.4. Air preheater

The air preheater is the last step of the boiler heat exchange path of the flue gasses. Thus, this step has two main purposes. The first one is to cool the gases before they are introduced to atmosphere in order to increase overall efficiency of the boiler. Another one is to heat up the air supplied to furnace for combustion. There are two types of air preheaters: regenerative and recuperative (Figure 2.10 and 2.11 correspondingly) [1, 5, 8].

The main principal of regenerative air preheater work is the indirect heat transfer from hot stream of flue gas to cold stream of combustion air without the solid conductive media. Thus, the mean of transfer media is performed by revolving rotor which is alternately heated and cooled by the flows. In the same time, recuperative air preheater directly transfers the heat between the hot and the cold flows via stationary conductive media. Usually, tubes and parallel installed plates play the role of exchanger in recuperative air preheaters [1, 5, 8].

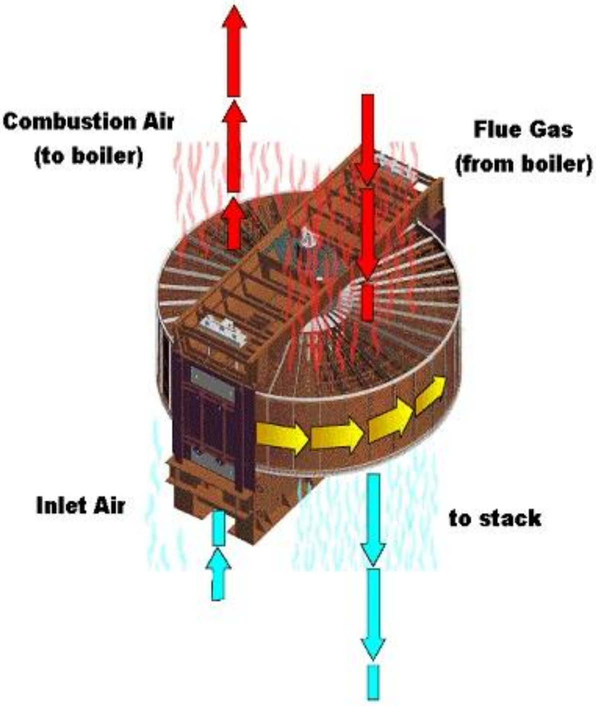

Figure 2.10. Regenerative air preheater [11].

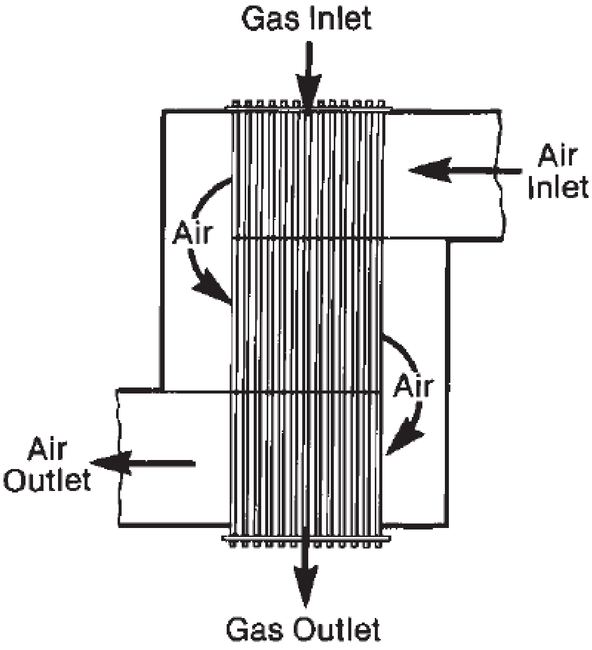

Figure 2.11. Recuperative three-pass vertical air preheater [5].

3. BOILER ENVIRONMENT

Boiler environment is a crucial part of boiler study. This concept encloses chemical and physical processes that take place inside the boiler such as fuel combustion, fouling and corrosion of heat transfer surfaces and heat distribution in different boiler parts. All these processes define conditions near different heat exchange surfaces affecting on the materials used in boiler design. Thus, it is necessary to know all these processes in case of material selection.

3.1. Fuel

The fuel can be considered as a finite resource of chemical potential energy in which energy stored in the molecular structure of particular compounds is released via complex chemical reactions [68].

3.1.1. Use of fuel

The share of fuels used in energy production is illustrated in Figure 3.1. It shows that 96.9 % of primary energy was provided by use of fuels as a source in 2009. But 91.1 % of primary energy produced by combustible types of fuel – fossil fuel and biofuel and waste.

Outlook in shares of energy sources in world primary demand is given in Figure 3.2. Different scenarios predict usage of different energy sources including combustible fuels by 2035. Current Policies Scenario assumes no change in government policies. New Policies Scenario takes into account existing policies and declared intentions. 450 Scenario assumes the average global temperature increase to 2° Celsius with corresponding changes in policies [13].

All scenarios show favorable future for combustible fuel. The worst scenario predicts approximately 80 % of its share in comparison to the best scenario with almost 90 % of share. Reducing of combustible fuel share describes by attempts to increase the use of renewable energy sources such as wind, solar, geothermal, and marine.

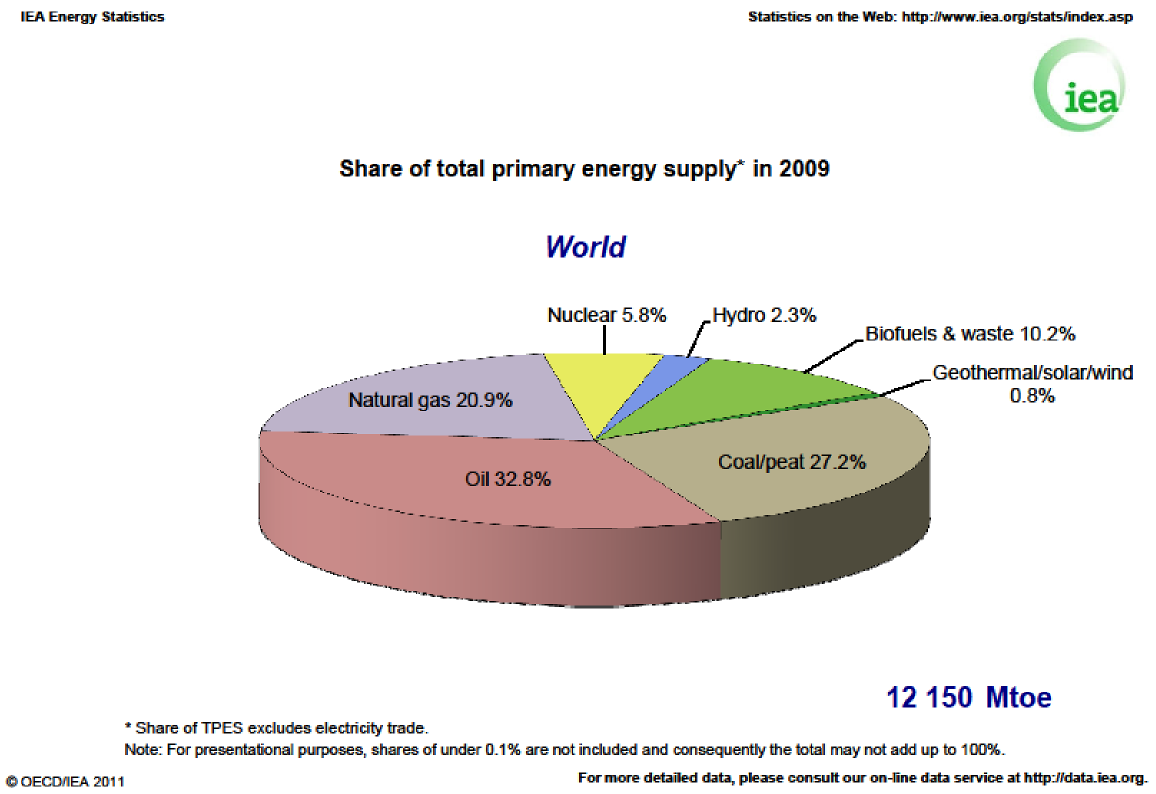

Figure 3.1. Share of total primary energy supply by sources [13].

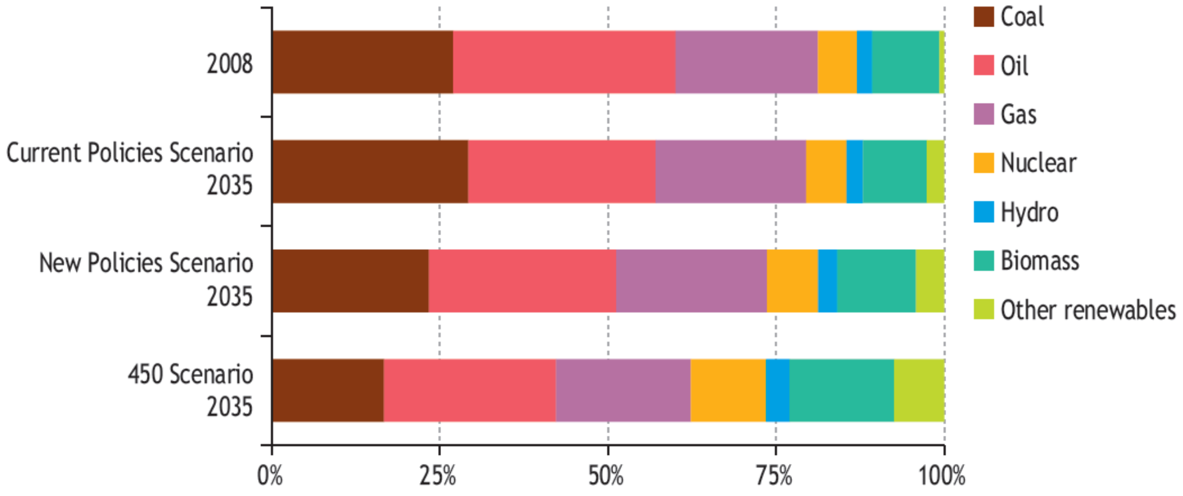

Figure 3.2. Shares of energy sources in world primary demand by scenario [14].

3.1.2. Fossil fuel

Fossil fuel is formed by natural anaerobic decomposition processes of buried dead organisms. The age of the organisms and thus fossil fuels is usually millions of years, and sometimes exceeds even hundreds million years. Also, fossil fuel is a non-renewable source of energy. Moreover, its reserve is limited and eventually is going to run out. Finally, fossil fuel cannot be renewed after once it has been mined [15]. Use of fossil fuel (coal/peat, oil and natural gas) has significant part in world energy production – 80.9 % (Figure 3.1). This fact proves that fossil fuel has been used as a pioneer for energy production, it is easy to produce comparing with other sources and technology of fossil fuel processing is well developed.

Fossil fuel can be classified by two different ways [15]. First one is based on physical state: solid, liquid and gaseous. Second is based on origin: natural, manufactured or byproduct. The classification matrix, which comprises all types of fossil fuels, is represented as Table 3.1.

Table 3.1. Classification of fossil fuels [15].

Natural	Manufactured or Byproduct
Solid	
Coal	Coke, coke breeze Coal tar
Lignite	Lignite char
Peat	
Liquid	
Petroleum	Gasoline Kerosene Fuel oil Gas oil Shale oil Petroleum fractions and residues
Gaseous	
Natural gas	Coke-oven gas
Liquefied petroleum gases (LPG)	Blast-furnace gas Producer gas Water gas Carburetted water gas Coal gas Regenerator waste gas

3.1.2.1. Solid

The major solid fossil fuel is the coal which has many forms due to its type, rank and grade. Types of coal depend on the age and they are following: anthracite, bituminous, sub-bituminous, lignite, peat. In this range peat is the first stage of coal formation and anthracite is the final. Nevertheless, different coals are heterogeneous mixtures form shiny black hard and brittle for the anthracite to yellow-brown soft and easy compressed for peat (Figure 3.3) [5, 15, 22, 68].

There are four main compounds of any coal: fixed carbon, mineral impurities called ash, water called moisture and volatile matter – gases released during coal heating. Composition of different types of coal is shown in Table 3.2 and content of the most interesting ash species is also presented in this table. Generally, the quality of coal changes with the time of transformation: the older is coal, the higher heating value. Additionally, heating value of coal is in the direct relation with fixed carbon content and in the inverse relation to moisture and volatile matter content. Finally, from all of the deposits peat is in the most concern of heat and power generation as the most common fossil within Finland. As the first stage of coal formation peat mass has high moisture content – about 70 % and ash content can widely vary from 2 to 70 % which both lead to low heating value (approximately 6980 kJ/kg), but sulfur content anyway remains the same low value – less than 1 % [5, 15, 68].

Another type of solid fossil fuel is coke, which is a residual which remains after coal, petroleum or tar pitch heating without access of oxygen (Figure 3.4). The main aim of coking process is to remove moisture and other volatile components giving an extremely carbon-rich material. Approximate compositions of different type of coke are shown in Table 3.2 [5, 15].

Table 3.2. . Basic elements in composition of fossil solid and liquid fuels causing problems related to polluting emissions and corrosion problems, wt%; M – moisture, A – ash [5].

Fuel	C	O	H	N	S	Cl	M	A	Ash composition					
									CaO	Na_2O	K_2O	MgO	P_2O_5	SO_3
Coals														
Anthracite (US)	83.7	2.3	1.9	0.9	0.7	-	7.7	10.5	0.60	0.74	2.65	0.30	-	1.38
Bituminous	83.1	9.5	5.0	1.3	1.1	0.04	3.1	15.7	4.90	0.77	1.61	1.55	0.22	2.16
Subbituminous	74.4	17.7	5.6	1.4	0.9	0.03	8.2	26.4	7.05	1.09	1.67	2.14	0.08	4.07
Lignite	64.0	23.7	5.5	1.0	5.8	0.01	10.5	34.6	13.11	0.48	1.48	2.50	0.20	8.64
Peat	56.3	36.2	5.8	1.5	0.2	0.04	14.6	3.9	9.97	0.10	1.12	2.14	2.75	12.11
Oils														
Light domestic fuel (Kerosine)	85.9-86.7	-	13.3-14.1	0-0.1	0.01-0.5	-	0.01-0.5	-	-	-	-	-	-	-
Medium domestic fuel	86.1-88.2	-	11.8-13.9	0-0.1	0.05-1.0	-	0.05-1.0	-	-	-	-	-	-	-
Very light residual	86.5-89.2	-	10.6-13.0	-	0.2-2.0	-	0.2-2.0	0-0.1	-	-	-	-	-	-
Light residual	86.5-89.2	-	10.5-12.0	-	0.5-3.0	-	0.5-3.0	0-0.1	-	-	-	-	-	-
Industrial fuel	86.5-90.2	-	9.5-12.0	-	0.7-3.5	-	0.7-3.5	0.01-0.5	-	-	-	-	-	-
Byproducts														
Coke breeze	80.0	0.5	0.3	0.3	0.6	-	7.3	11.0	-	-	-	-	-	-
Petroleum coke	71-88	-	-	0.4	1.2	-	3-12	0.2-3.0						
Coal tar pitch	90.1	0.6	4.9	0.6	0.9	-	2.2	0.7						

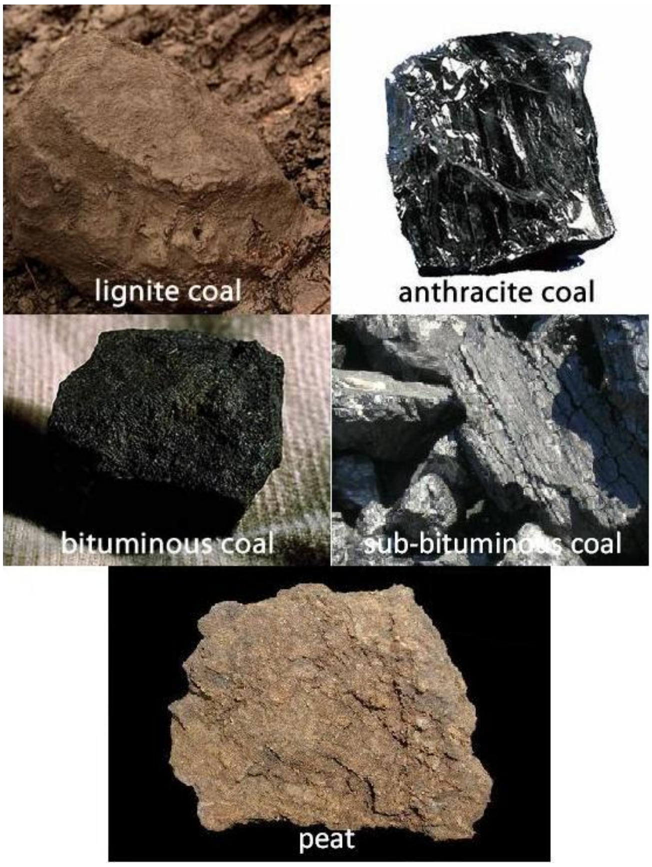

Figure 3.3. The main types of coal [23-25].

Figure 3.4. Types of coke [26-28].

3.1.2.2. Liquid

Liquid fuel is represented not by crude oil itself, but by range of fuels as its derivatives. Generally, petroleum is a mixture of paraffinic, naphthenic and aromatic hydrocarbon, additionally contain small amount of sulfur, nitrogen and oxygen. Due to the complex composition it can be refined by distillation process to obtain range of liquid fuels with different combustion properties (Figure 3.5). Usually, fuel oil used for the steam and heat generation in industrial boilers is heavy products of crude oil processing [22].

Figure 3.5. Test tubes of various products obtained from crude oil. Fractions are arranged in order of boiling point from left to right (highest to lowest): bitumen, fuel oil, heavy, medium, light lubricating oils, diesel, jet fuel (kerosene), and petrol (gasoline) [29].

Petroleum fuels differ from each other by the weight of the fraction and thus by volatility and the flush point. The lighter a fuel, the most volatile it is and thus the easiest to burn. Moreover, heavy types are the most contaminated and contain small amount of ash (not exceed 0.5 wt%, see Table 3.2) in form of alkali metal oxides – sodium and potassium (Na_2O and K_2O), alkaline earth metal oxides – magnesium and calcium (MgO and CaO) and non metallic oxides – phosphorous and sulfur (P_2O_5 and SO_3). While light fuels are clean – ash free and have low viscosity giving such a good combustion behavior. Also, all listed properties cause the difference in heating value, where heat value increase in the range from heavy to light fuels. Light fuels can also be used in power generation, but their usage is limited by their high cost. Thus, they are mostly used in cases where easily burn and ash free fuels are needed such as ignition, maintain of burning, etc. [5, 15, 30, 98].

3.1.2.3. Gaseous

The main gaseous fossil fuel is the natural gas. Natural gas is a mixture of hydrocarbon compounds with some small additions of non-hydrocarbon matter existing in the gaseous phase. Principal hydrocarbon components are methane, ethane, propane, butanes and pentanes. Non-hydrocarbon gases are usually carbon dioxide, helium, hydrogen sulfide and nitrogen [5, 15, 22].

Additionally, refinery and oil gas produced by thermal treatment of coal (destructive distillation, partial combustion) and petroleum (distillation, cracking) is also can be considered as gaseous fuel for power generation. Moreover, gaseous fuel is the most desirable for steam generation from all fossils because it is free of ash and easily forms burn mixture with air. Also, it can be easily transported directly to the consumer by piping without need of storage [5, 15].

3.1.3. Renewable biomass

The most general definition of biomass is the biodegradable fraction of products, waste and residues from biological origin from agriculture (including vegetal and animal substances), forestry and related industries including fisheries and aquaculture, as well as the biodegradable fraction of industrial and municipal waste. Biomass is a renewable type of energy due to the fact that new trees, plants and crops can be grown after burning old ones and new portions of waste will appear because of the human and animals activity [16, 17].

Use of biomass and waste in world energy production take notable part – 10.2 % (Figure 3.1). All scenarios described by Figure 3.2 show increase of biomass share in energy production even in the worst case for combustible fuels. It can be described by list of advantages of biofuels such as: greenhouse gas and other air pollutant reductions, energy cost savings, local economic development, waste reduction and security of a domestic fuel supply [18].

Biomass can be classified by different methods. General way divides biomass on woody and non-woody [19]. Naturally biomass is classified by its origin: woody, herbaceous, fruit, blends and mixtures [20]. More convenient way to classify biomass by origin due to economic sector: forestall, agriculture, industrial, urban [16, 21]. In this overview it seems useful to use the last classification, but in following manner: woody, agriculture, waste and byproducts (Table 3.3) [31-34].

Table 3.3. Classification of fuel biomass [32].

Woody	
Solid	Fuel wood (wood in the rough, chips, sawdust, pellets), charcoal
Liquid	Black liquor, methanol, pyrolitic oil
Gas	Gasification and pyrolisis products of listed fuels
Agriculture	
Solid	Straw, stalks, husks, bagasse, charcoal from the above fuels, dried dung

Liquid	Ethanol, raw vegetable oil, oil diester, methanol, pyrolytic oil from solid agrofuels
Gas	Biogas, producer gas, pyrolisis gases from agrofuels
Waste and byproducts	
Solid	Municipal solid wastes (MSW)
Liquid	Sewage sludge, pyrolitic oil from MSW
Gas	Landfill gas, sludge gas

Thereby, the biomass is represented by huge range of constituents such as different wood families including residuals and different semi products (bark, chips, black liquor, etc.), crops, animal wastes and manures, humanity wastes and sewages. As a result, this variety causes fluctuations in chemical composition (see Table 3.4) even in the same type of biomass and depends on original conditions (age, chemical activity, absorbing capacity, inclusions and additives, logistics) [40].

3.1.3.1. Woody

Woody biomass is a plant material from trees and shrubs that can include roots, bark, leaves, branches, limbs, trunks and vines. The origin of woody biomass is various and can be represented by many sources, including forestry operation residues, wood product residues, urban waste wood, trees grown specifically for energy, fuelwood and forest cutting that reduces damage caused by fires and pests (Figure 3.6) [35-37].

The four major components of woody biomass are cellulose, hemicellulose, lignin and mineral components. Here, cellulose is a polymer composed of glucose chains, hemicellulose consists of pentose sugar carbohydrates and lignin is a phenylpropane polymer. Thus, woody biomass mainly consits of carbon, hydrogen and oxygen. Additionally, mineral components mainly consist of carbon, hydrogen and oxygen, but they are also include nitrogen, sulfur, chlorine, alkali compounds such as sodium and potassium (see Table 3.4), heavy metals [37-39, 41]. Finally, moisture of woody biomass varies greately and can reach values up to 50 % [57, 63, 64].

Figure 3.6. Types of woody fuel [38, 44, 45].

3.1.3.2. Agricultural

Agricultural biomass is a relatively broad category of biomass that includes: the food-based portion of crops (such as corn, sugarcane and beets), the nonfood-based portion of crops (such as corn stover (the leaves, stalks and cobs), orchard trimmings and rice husks), perennial grasses, and animal waste (Figure 3.7). Additionally, agricultural biomass is usually available at one time of year, while woody can be harvested whole year round. Also, the annual yield from cropland is approximately 20 times less than average stock of biomass on forest land. Therefore, costs associated with processing of most agricultural residues are high and agriculture fuel does not widely used for energy purposes. Nevertheless, it can be a significant biomass source if technology and infrastructure will be developed to meet economical recover and deliver of agricultural biomass to firing sites [42, 43].

Table 3.4. Basic elements in composition of biomass causing problems related to polluting emissions and corrosion problems, wt %; M – moisture (as measured), A – ash (dry basis) [40].

Biomass	C	O	H	N	S	Cl	M	A	Ash composition					
									CaO	Na_2O	K_2O	MgO	P_2O_5	SO_3
Woody														
Pine chips	52.8	40.5	6.1	0.5	0.09	0.06	7.6	6.0	7.89	1.20	4.51	2.43	1.56	1.19
Sawdust	49.8	43.7	6.0	0.5	0.02	-	34.9	0.7	44.11	2.48	10.83	5.34	2.27	2.05
Spruce wood	52.3	41.2	6.1	0.3	0.10	0.01	6.7	0.5	17.20	0.50	9.60	1.10	1.90	2.60
Wood residue	51.4	41.9	6.1	0.5	0.08	0.05	26.4	5.4	11.66	4.47	4.85	3.06	1.37	1.99
Crops and herbaceous														
Rice husks	49.3	43.7	6.1	0.8	0.80	0.12	10.6	18.0	0.97	0.16	2.29	0.19	0.54	0.92
Straw	48.8	44.5	5.6	1.0	0.13	0.54	12.4	10.8	6.70	0.70	25.82	1.67	2.74	3.89
Sunflower husks	50.4	43.0	5.5	1.1	0.03	0.10	9.1	3.1	15.31	0.80	28.53	7.33	7.13	4.07
Switchgrass	49.7	43.4	6.1	0.7	0.11	0.08	11.9	5.1	10.21	0.58	9.64	4.71	3.92	0.83
Animal														
Chicken litter	60.5	25.3	6.8	6.2	1.20	0.50	9.3	37.8	56.85	0.60	12.19	4.11	15.40	3.59
Meat-bone meal	57.3	20.8	8.0	12.2	1.69	0.87	2.5	24.0	41.22	6.41	3.16	1.38	40.94	4.24
Waste														
Greenhouse-plastic waste	70.9	16.4	11.2	1.5	0.01	0.05	2.5	31.8	25.80	0.80	9.70	5.70	3.84	2.65
Mixed waste paper	52.3	40.2	7.2	0.2	0.08	-	4.2	26.1	7.63	0.54	0.16	2.40	0.20	1.73
Refuse-derived fuel	53.8	36.8	7.8	1.1	0.47	0.83	6.4	46.3	26.81	1.36	0.23	6.45	0.77	3.01
Sewage sludge	50.9	33.4	7.3	6.1	2.33	0.04	38.1	20.4	13.04	2.25	1.60	2.49	15.88	2.05

Figure 3.7. Types of agriculture fuel [46-50].

In general, agriculture biomass is more challenging than the woody one. This explains by lower bulk density and higher content of chlorine, potassium, nitrogen, magnesium and phosphorous especially for straw and different husks in comparing with wood and forestry waste fuel (see Table 3.4). Additionally, agricultural biomass have moisture content from less than 20 % for agricultural wastes (husks, straws, etc.) up to 60 % for bagasse and even above 85 % for animal manure [61, 63, 64, 107].

3.1.3.3. Waste and byproducts

Waste and by products consist of big group of waste represented by municipal solid waste (MSW), sewage sludge and their derivatives (Figure 3.8). The biomass resource in MSW comprises the putrescibles (decomposable organic waste, can include food waste, used diapers, and pet waste [66]), paper and plastic and represents 80% of the total collected MSW [65].

Figure 3.8. Types of waste fuel [51, 52].

Sewage sludge is a source of biomass energy very similar to the animal wastes [65]. The sludge concentrates heavy metals and poorly biodegradable trace organic compounds. It is rich in nutrients such as nitrogen and phosphorous and contains organic matter. Example of chemical composition of different wastes and byproducts can be seen in Table 3.4 [67].

3.2. Combustion

Combustion is defined as the exothermic oxidation process of combustible elements of a fuel to produce useful heat energy. There are three main combustible elements in most fuels: carbon, hydrogen and sulfur. All of these constituents are burned to corresponding oxide: carbon dioxide (CO_2), water vapour (H_2O) and sulphur dioxide (SO_2). Also small amounts of sulfur trioxides (SO_3), nitrogen oxides (NO_x) and unburned hydrocarbons can be formed [1, 5, 15, 98].

3.2.1. Theory of combustion

Mechanism of combustion process is based on the oxidizing reactions (Table 3.5). Initially, combustion takes place in gaseous (homogeneous) phase due to release of volatile hydrocarbons and maintains flame stability. Then combustion of nonvolatile residue (char or coke concerning oils) starts. Gaseous oxygen reacts with solid carbon forming releasable carbon oxide or dioxide. However, combustion of nonvolatile matter goes slowly comparing with rapid initial volatile stage. Thus, char particles burn through the whole fluidized layer and even can leave bed being unburned [1, 5, 53].

Table 3.5. Common chemical reaction of combustion [5, 15].

Combustible	Reaction	Heat of combustion, MJ·kg^{-1}
Carbon (to CO)	$2C + O_2 = 2CO$	9.22
Carbon (to CO_2)	$C + O_2 = CO_2$	32.76
Carbon monoxide	$2CO + O_2 = 2CO_2$	10.09
Hydrogen	$2H_2 + O_2 = 2H_2O$	141.86
Sulfur (to SO_2)	$S + O_2 = SO_2$	9.25
Methane	$CH_4 + 2O_2 = CO_2 + 2H_2O$	55.53
Acetylene	$2C_2H_2 + 5O_2 = 4CO_2 + 2H_2O$	49.93
Ethylene	$C_2H_4 + 3O_2 = 2CO_2 + 2H_2O$	50.31
Ethane	$2C_2H_6 + 7O_2 = 4CO_2 + 6H_2O$	51.91
Hydrogen sulfide	$2H_2S + 3O_2 = 2SO_2 + 2H_2O$	16.49

A particle of solid fuel injected into a FB undergoes the following steps: heating and drying, devolatilization and volatile combustion, swelling and primary fragmentation (for some types of coal), combustion of nonvolatile matter (char) [1, 5, 53]. These processes are shown in Figure 3.9, which represents the order of magnitude of time taken by each step.

Combustion of liquid fuel consists of heating, drying, devolatilization (evaporation), combustion of volatile matter and combustion of nonvolatile residual (coke). However, gaseous fuel differs from combustion of solid and liquid fuel due to absence of ash forming part. Thus, combustion of gas consists just of heating and combustion of gas-air mixture due to existence of fuel already in the desired state [5, 53, 98].

The common source of oxygen for combustion in boiler practice is air. In the same time air is a mixture of nitrogen, oxygen and small amounts of water vapor, argon and other elements. However, big content of nitrogen in the combustion air reduces combustion efficiency by absorbing heat obtained from the combustion and diluting the flue gases. These cause reducing of heat available at heat exchange surfaces and increasing of combustion products volume [1, 5, 15, 30, 53].

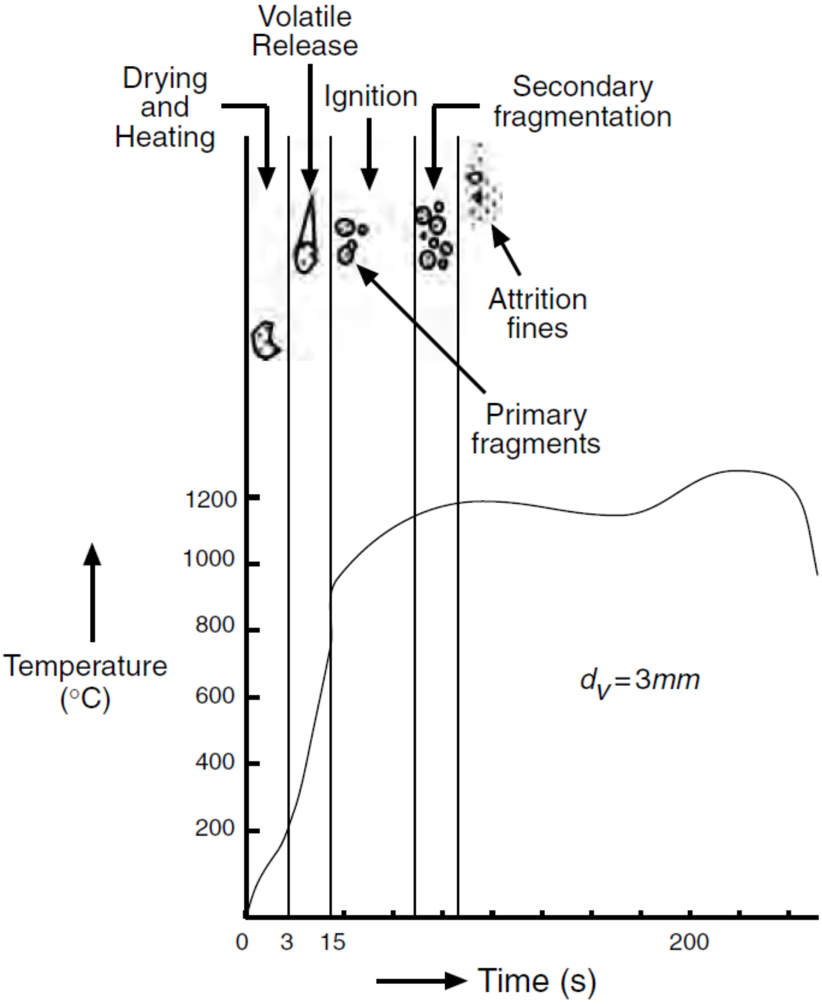

Figure 3.9. Stages of particle burning (d_v – diameter of initial fuel particle) [1].

To provide complete combustion of fuel components with corresponding products as it is shown in Table 3.5 the stoichiometric or theoretical amount of oxygen is required. In practice some differences from ideal case are appeared. When, for example, fuel contain oxygen by itself, the less amount of theoretical oxygen/air is required. And also, mixing between fuel and air is never perfect thus, extra oxygen is provided in furnace in the form of excess air [1, 5, 15, 98].

Finally, combustion of nonvolatile residual (char or coke) releases noncombustible inorganic inclusions called ash, which can be classified on bed and fly ash. Bottom ash is coarse particles removed directly from the bed or furnace, while fly ash is fine particles entrained by gas flow. However, amount and reactivity of ash depends on initial fuel composition and structure [1, 5, 15].

3.2.2. Factors affecting combustion efficiency

Generally factors affecting on combustion efficiency of boiler can be divided in three categories: fuel characteristics, operational parameters, design parameters. Characteristics of fuel noticeably influence on combustion efficiency are listed in Table 3.6. Table 3.7 describes operating conditions leading to changes in combustion efficiency. Finally, design parameters are related to bed height, freeboard height, recirculation of combustible losses, fuel feeding, secondary air injection [1, 5].

Table 3.6. Fuel characteristic factors affecting on combustion efficiency [1, 54, 56, 57, 65].

Characteristics of fuel	Description
Fuel ratio	It represents ratio of fixed carbon to volatile matter content. Higher values lead to lower combustion efficiency
Particle size	Attrition, fragmentation, swelling, size of fuel particle have influence on combustion efficiency in the same way. Fine particles increase loss of unburned fuel and sorbent, create additional load on filtration system and alter particle distribution. Thus decrease combustion efficiency
Internal reactivity	More reactive fuels have higher combustion efficiency
Volatile matter and devolatilization	Volatile matter burns faster than char causing lower combustion efficiency by increase in release of CO from the furnace
Ignition	The lower the ignition temperature, the shorter the startup time and the lower consumption of additional fuel

Table 3.7. Operating condition factors affecting on fuel combustion efficiency [1, 5, 56 ,59]

Operating conditions	Description
Fluidized velocity	Increasing of fluidized velocity leads to decrease of combustion efficiency due to higher yield of unburned fines and oxygen bypassing
Excess air	Excess of no more than 20 % of air increases combustion efficiency
Combustion temperature	Higher temperature increases combustion of fines and thus total efficiency

3.2.3. Combustion of fossil fuel

Combustion of fossil fuels types in fluidized bed boiler is followed by problems of combustible losses. Mostly these problems are related to coal due to higher ash content comparing to oil and gas. Forms of these losses are unburned char particles carried away by both bed and fly ash and carbon monoxide. That is why in order to increase combustion efficiency of fluidized bed recirculation of ash is used. However, just fly ash is sent back for reburning due to high content of unburned carbon in it (up to 10 %) comparing with bottom ash. Low operating temperature of fluidized bed does not cause any significant problems as in coal-fired power plants using pulverized or cyclone furnace boilers [1, 5, 98].

3.2.4. Combustion of biomass

The main ways of biomass utilization are combustion of single biomass and co-firing with fossil fuel. However, just indirect co-firing of biomass uses fluidized bed combustion represented by circulating bed. Biomass is burned separately from coal fired unit providing gasification and obtained gas is further fed to coal boiler furnace. Biomass can substitute up to 20 % of the coal used in boiler which leads to direct reduce of sulfur dioxide, nitrogen oxides emissions and green house gases such as carbon dioxide and methane [12, 18, 60-62].

Biomass is more reactive than fossil fuel and combustion (oxidation) is not a main issue. However, bed sintering, slagging, fouling and corrosion during the combustion caused by biomass composition are the general problems. These challenges are caused by relatively high chlorine, alkali metals (sodium and potassium), heavy metals (zinc, lead, vanadium) content. Some effects on boiler environment caused by elements in composition of biomass are listed in Table 3.8 [1, 5, 40, 55, 56, 58, 64].

Table 3.8. Effect of biomass fuel composition on boiler performance.

Elements	Effect
Alkali Metals	Bed agglomeration Slagging Fouling High temperature corrosion
Chlorine	Bed agglomeration Slagging Fouling High temperature corrosion

	HCl emission Dioxin formation
Heavy Metals	Slagging High temperature corrosion Emissions
Sulfur	High temperature corrosion Dew point corrosion SO_2 emission
Phosphorous	Bed agglomeration Slagging Fouling
Nitrogen	NO_x emission

High volatile content (60-80 %) makes combustion relatively low in the lower bed and eliminates additional heat extraction by immersed tubes. Also, high moisture content (10-65 %) increases the flue gas volume per unit heat release which causes bigger cyclone and by-pass parts. Furthermore, content of oxygen in biomass is very high (30-40 %) comparing with fossil fuel and leads to less consumption of excessive combustion air and further to reduction of flue gas volume [1, 40, 57].

Summarizing, the challenges associated with different ranks of fuel fired in fluidized bed are shown in Figure 3.10. The challenges are related to different fuel factors such as preparing demand of the fuel, heating value and corrosion potential [6, 7].

3.3. Slagging and fouling

Slagging and fouling are both processes related to formation of deposits on heat transfer surface. Further, this depositions decrease heat transfer and induce corrosion of covered boiler parts. However, they have different mechanisms: slagging is the formation of deposits on surfaces exposed to radiant heat such as furnace walls or high temperature gas flow due to melting of ash. While fouling is the formation of bonded deposits (sintered or cemented) on convection heat transfer surfaces not exposed to radiant heat such as superheater and reheater. It can also be formed on furnace wall at temperatures low enough not to provide melting. Formation of bonded deposits is possible due to condensation of volatile inorganic compounds vaporized during combustion [1, 5, 15].

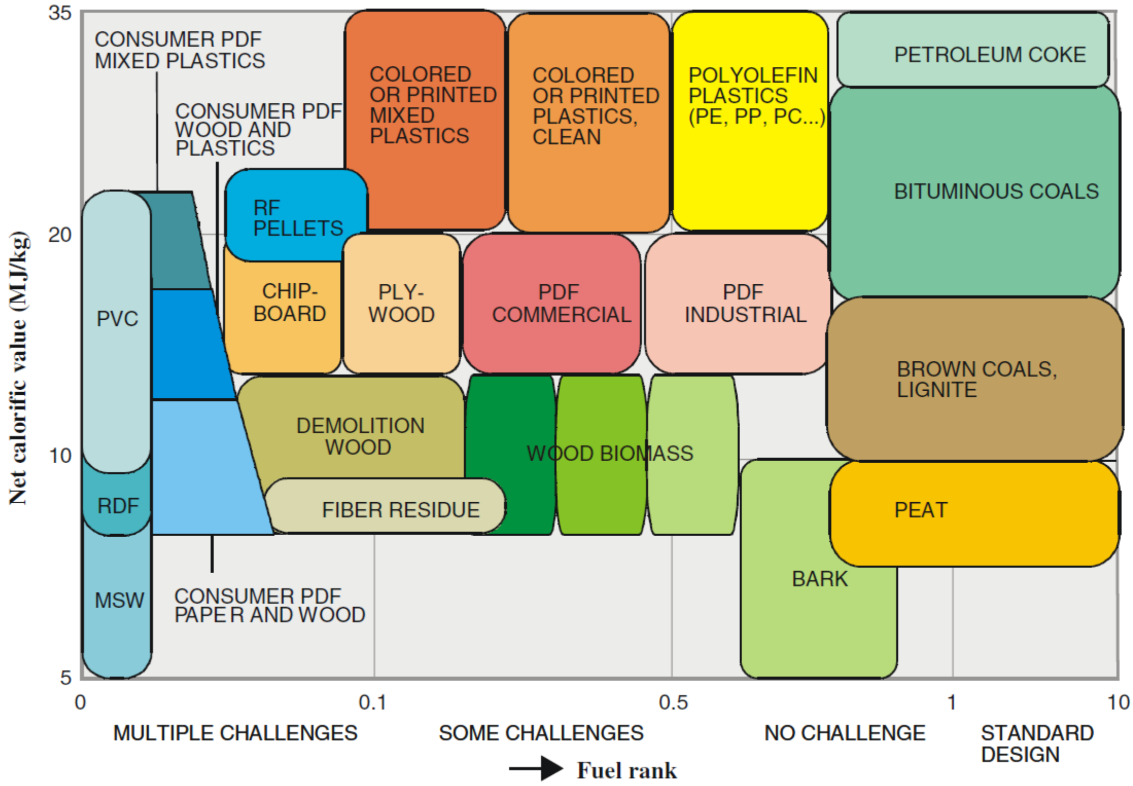

Figure 3.10. Utilization challenges related to the rank of fuel utilized in FBC technology [6]; PVC – polyvinyl chloride, RDF – refuse derived fuel, MSW – municipal solid waste.

Fly ash particles become sticky due to softening or melting at high combustion temperatures and cover heat transfer surfaces such as water walls, superheaters and reheaters. They settle down and solidify on tube surface due to low temperature comparing with flue gas. However, sticked ash layer cracks and some fraction of particles returns back to the gas flow. Nevertheless, within the time stable cover is formed due to deposition of fine particles or low melting compounds. And when thickness of deposit reaches level, when outer layers melt due to high temperature above the tube surface, the process becomes self-accelerating. Molten deposits are able to catch and accumulate other fly particles [5, 15, 98].

3.4. Corrosion

3.4.1. Corrosion mechanisms

Corrosion is the process of returning materials into their thermodynamically stable forms via electrochemical reaction. Usually, these forms are represented by oxides and sulfides. Nevertheless, electrochemical mechanism remains the same to any type of material and consisted of two parts: anodic and cathodic [80, 108, 109].

Anodic process is an oxidation of metal to higher valence state and thus provides dissolving (corrosion) of metal. Cathodic process is difficult to predict but the list of possible reactions is defined as follows: hydrogen evolution, metal ion reduction and/or deposition, oxygen reduction in neutral and acid solutions. Both of the parts exchange electrons and induce electrical potential difference between them. Finally, electrical circuit is formed, where electrons current flows from anode to cathode [80, 108, 109].

Difference of potential between anode and cathode is the driving force of corrosion process. Thus, corroding metal surface can be observed as a system of small cells with anode and cathode zones. Formation of these simple cells is a result of heterogeneities at the metal interface. Main types of electrical cells leading to different corrosion mechanisms are: dissimilar electrode (galvanic) cells, concentration (oxidation) cells, differential temperature (stress) cell [80, 108, 109].

Different mechanisms of corrosion result in variety of corrosion types: general (uniform) corrosion, crevice corrosion, pitting corrosion, intergranular corrosion, galvanic corrosion, stress corrosion cracking (SCC), erosion corrosion (exfoliation), corrosion fatigue, hydrogen damage. All listed types and their essence are briefly described in Table 3.9 [80, 108, 109].

Table 3.9. Corrosion mechanisms and their definition [1, 15, 80, 108, 109].

Type of corrosion	Mechanism
Uniform	Chemical attack or dissolution of a metal and/or corrosion products
Crevice	Localized corrosion in areas formed by contact between a metal and a non metal (gaps and openings)
Pitting	Highly localized loss (attack) of a metal
Intergranular	Corrosion attack at the grain boundaries of a metal
Galvanic	Corrosion of dissimilar coupled metals
Exfoliation	Removal of scale or corrosion product by erosion of gaseous or aqueous flow
SCC	Cracking of the alloy dew to simultaneous action of corrosive environment and static tensile stress
Corrosion fatigue	Cracking of the alloy dew to simultaneous action of corrosive environment and repeated tensile stress
Hydrogen damage	Degradation of mechanical and physical properties dew to action of hydrogen

Power boilers have two neighboring types of surfaces and corrosion optional for each of them. First is related to surfaces coupled with combustion of fuel and conventional pass of flue gas named fire side corrosion. Another type is related to boiling of water and steam generation named water/steam side.

Water/steam side corrosion is limited to crevice, pitting, intergranular and stress corrosion cracking. Typically corrosion of water circuit of boiler is a result of simultaneous action of stress and chemical reactions related to feed water quality – presence of impurities, non uniform content of water stream (salts, oxygen). These problems are not as challenging as in fire side and can be eliminated by appropriate water treatment and operation [1, 5, 108, 109].

3.4.2. Fire side corrosion

Commonly, fire side corrosion of boiler parts is represented by following types: macro pitting (uniform corrosion of big areas), crevice, intergranular corrosion, stress corrosion cracking. Cause of corrosion is related to highly reactive fly ash content of fuel, uncontrollable combustion, high temperature, non uniform atmosphere, erosion. Oxidation related to scaling and deposits formed by ash stand for the ways of fireside corrosion [1, 5, 80, 109].

3.4.2.1. Scaling

Interaction metal with flue gases on fire side provides protective oxide scale dew to diffusion resistance. Thus, oxidizing of steel surface is not so deep and decrease with time (time-dependant tendency is well known and presented e.g. in [15]). But scaling also causes metal wastage by exfoliation which provides rapid oxidation of bare unprotected steel. And thus, cyclic scale formation and removal reduce wall thickness and as a result failure of steel is occurred [1, 15, 105, 109].

3.4.2.2. Ash corrosion

In general, ash corrosion induced by different elements is coupled with the same mechanism. Thus, depositions on the tube surface form melt, which dissolves protective oxide layer and further accelerate corrosion. Further, reduction atmosphere inhibits creation of protective oxides on the bare surface and leads to formation of porous non protective compounds.

Chemical mechanism of these processes is shown on Figure 3.11. Chlorine plays the most crucial role in inducing and maintaining of ash corrosion [1, 5, 104, 105, 120].

Sulfur. Due to low temperature of combustion in fluidized bed boilers just two ways of corrosion involving sulfur are possible: sulfate and sulfide induced corrosion. Sulfate corrosion is possible when burned fuel contain alkali metals - both they form alkali sulfates. Sodium and potassium sulfates evaporate at temperatures above 900 °C and than condensate (dew point is about 870 °C) on relatively cold heat exchange surfaces. Further, this condensate reacts with protective oxide layer of tubes and form non protective complex sulfates. When thickness of sulfate deposits becomes high enough to melt complex sulfates dissolving (acidic dissolving) of protective oxide is occurred. In addition to complex sulfates, alkali pyrosulfate is another compound forming melts at relatively low temperatures [1, 5, 104, 105, 107].

Sulfide corrosion takes place in reducing conditions where alkali metals together with sulfur oxides form sulfides. Another cause is hydrogen sulfide which reacts with metal oxide on the heat exchange surface. As a result porous and thus non-protective metal sulfide is formed and further again transforms to oxide but as a sulfide it is porous and non protective [1, 5, 104, 105, 107].

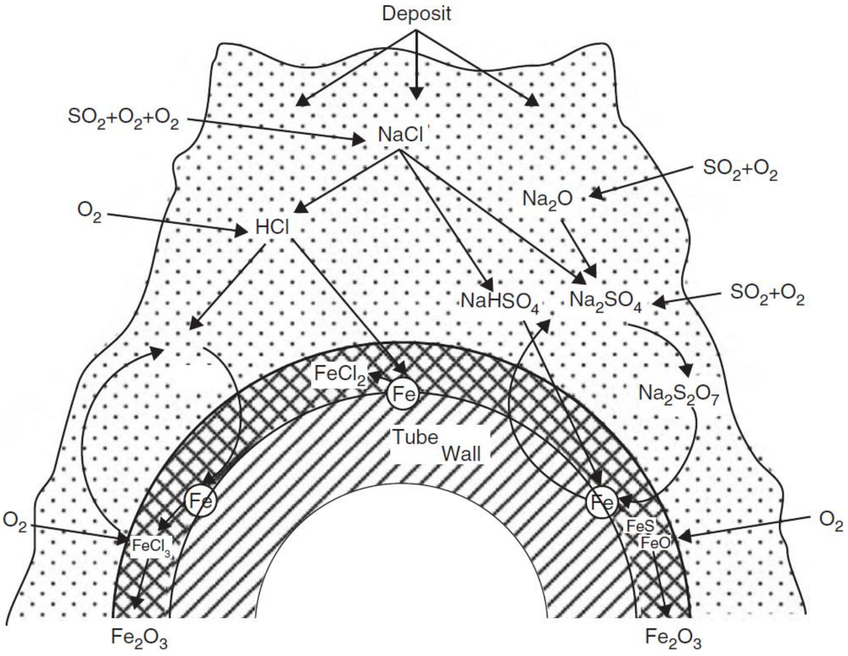

Figure. 3.11. Chemical mechanism of ash corrosion [1].

In addition to ash corrosion sulfur also provides *dew-point corrosion*. Thus, sulfur dioxide, sulfur trioxide and water vapor this gas mixture has dew point around 150 °C. Condensate is represented by sulfuric and sulfurous acid, which tend to form on economizer, air preheater surfaces. Condensation of hydrochloric acid is also possible but dew point of hydrochloric gas is about 54 °C. Presence of fly ash adds negative effect - it forms sponge deposits collecting acidic gases and moisture [1, 5, 15, 98, 105].

Chlorine. Combustion of high chlorine fuel especially in combination with high alkali metals provides accelerated corrosion and can involve gaseous, molten and solid phase. The mechanisms of chlorine-induced corrosion are following. Gaseous chlorine or chloride from the flue gas diffuses through pores and cracks in deposits and scales. At the metal-oxide interface in the absence or low partial pressure of oxygen it reacts with base metal of the tubes and provides volatile at high temperature metal chlorides. Then vapor chlorides diffuse to the gas-scale interface and oxidized due to high partial pressure of oxygen forming non or low protective metal oxide deposits and gaseous chlorine. Further, part of this gaseous chlorine again penetrates through protective scale and reacts with iron in the same way. Thus, chlorine acts as a catalyst in this corrosion mechanism [1, 104, 105, 106, 107].

Alkali, alkaline earth and even some heavy (e.g. zinc, lead) metals accelerate the corrosion involving liquid phase which is related to low melting point of chlorides (150-500 °C as it listed in [104]). Thus, molten chlorides of alkali metals cover surface of tubes and dissolve protective metal oxides by formation of basic salts (e.g. $NaCrO_2$, $(Na,K)_2CrO_4$,) and make bare metal layer attractive to further oxidation. Additionally, chlorine released during accelerating reactions is another source of gaseous chlorine involved in cyclic reactions of metal waste [104, 105, 106, 107].

Potassium chloride is in the most concern regarding to ash deposit corrosion. Use of fertilizers determines high content of potassium especially in agriculture biomass comparing to other corrosive impurities even sodium (see Table 3.4). That is why, combustion of biomass is related to severe corrosion of superheaters/reheaters caused by potassium. And relatively high content of chlorine (Table 3.4) gives volatile and low melting potassium chloride. Actually, potassium chloride interacts with protective oxide scale and dissolves it releasing chlorine – the main causer of metal waste (the mechanism of this process is described above - sub-sub chapter *Chlorine*).

3.4.3. Corrosion of non ferrous alloys (beneath salt depositions)

Essentially ferrous alloys and materials that, which contain iron as base metal in their composition are not corrosion resistive. The nature of iron oxides formed during corrosion process is porous, weak, brittle and denser comparing to the iron itself. On the other hand oxides of some non ferrous metals meet the whole properties to form corrosion protective oxide scale. Thus, the oxides of nickel, chromium, cobalt and plenty of other non ferrous metals are tight with good mechanical properties which give them and materials with their additions well know excellent resistivity [120].

Nevertheless, non ferrous alloys applied in boiler environment are experienced high temperature, severe inhomogeneous oxidative gaseous atmosphere (with inclusions of reduction zones) and highly corrosive salt depositions which were described previously (see section 3.4.2.2.). All these factors make non ferrous metals and alloys susceptible to hot or deposit corrosion and can be described by two general mechanisms. The first is coupled with the material dissolution caused by solubility of the metal/alloy and its oxide in molten salt depositions. The second mechanism involves the oxidation of the metal to ions by sediment salts and their molten solutions and is the most common way of metal material waste [119].

In such a way, the main causes of non ferrous materials failures are following. First of all, it is a chemical dissolution of the protective oxide scale accelerated by presence of salts providing general corrosion (oxidation). Next cause is a selective leaching of more soluble impurities in the bulk material which results in severe localized corrosion (e.g. pitting, crevice) and intergranular corrosion by depletion of non ferrous metals content at the grain boundaries. Also, intergranular corrosion can be enhanced by difference in structure and thermomechanical treatment of the material. Finally, rapid local corrosion can be caused by initially weak oxide scale or damages occurring during operation, otherwise just slight general corrosion can be observed [120].

Thereby, for desired long service of the designed object the material should be selected in that way to form passive oxide layer which in not soluble in the expected melt. Additionally, the temperature of the material surface should be as low as possible in order to decrease the diffusion rates inside the formed melt and reduce the solubility of protective scale [119].

4. NON FERROUS MATERIALS

Material selection is the most important part of boiler design. Correctly used materials help to achieve maximum levels of safety, efficiency and lifetime of boiler in case of high economical efficiency. Thus, choice of material synergistically depends on range of factors: cost, performance factors (heat transfer area, steam temperature, mass flow), mechanical factors (pressure, design temperature, thermal and mechanical stresses), environmental factors (corrosion and erosion resistance), manufacturing limitations (weldability, bending, etc.). Where cost is the major factor influencing on last decision [5, 70].

Heat and power generation processes involving biofuel and waste utilization provide high temperature off gas flow combined with extremely corrosive content. This sets new challenges for the materials applied in pressure parts. And force to search reliable materials resistive against high temperature corrosion and cracking and in the same time having acceptable price and costs.

4.1. Requirements and legislations

Pressure vessels are operated at high pressure and temperature and thus, should be manufactured in order to maintain safely usage. Otherwise, inadequately designed equipment causes significant hazard. Thus, lots of attention should be paid for design and materials of pressure parts to provide high level of safety. To meet this point design codes were established to govern design and material certification of pressure vessels. Such codes can be represented by universally accepted ASME Boiler and Pressure Vessel Code (BVPC) in North America and the Pressure Equipment Directive (PED) of the EU is obligatory within the EU countries since 30 May 2002. By listing the allowable stresses for the certified materials, these codes limit the materials that can be applied in construction. However, the final chose of the materials is the responsibility of engineers [82, 83].

4.1.1. Boiler and Pressure Vessel Code

The ASME Boiler and Pressure Vessel Code Subcommittee on Materials identifies and approves materials and their specifications which are considered for utilization in boiler and pressure vessel construction. Also they gain acceptable design values of materials as a function of temperature. Boilers with steam pressure more than 100 kPa and high temperature water boilers with operation pressure exceeding 1.1 MPa and/or temperature exceeding 120 °C are designed following to Section I of the Code, *Rules for Construction of Power Boilers*, which lists specifications of approved materials. Texts of specifications are presented in Section II, Part A, *Ferrous Materials Specifications* and Section II, Part B, *Nonferrous Materials Specifications*. In addition Section II, Part D, *Properties* contains design values including allowable stresses and welding requirements notes of those materials. Finally, Section II, Part C, *Specifications for Welding Rods, Electrodes, and Filler Metals* includes approved materials for welding [5, 82, 84].

4.1.2. Pressure Equipment Directive

The Pressure Equipment Directive 97/23/EC of the EU provides unification of national laws of Member States in order to ensure free placing of pressure equipment on the European market without any legislation barriers. Annex I, *Essential Safety Requirements* presents general, design, materials and manufacturing requirements for pressure equipment defined in Article 3 of PED. In addition, PED materials for pressure equipment must satisfy one of the following requirements: comply with a Harmonised Standard Material, be covered by a European Approval of Material (EAM) or particular material appraisal (PMA). Harmonised Standards produced by European Committee for Standardization (CEN) represent materials, products and methods matching desirable level of safety for pressure equipment via EN 13445:2002, *Unified Pressure Vessels*, EN 13480:2002, *Metallic Industrial Piping*, EN 12952 and EN12953, *Water-tube and Shell Boilers* standards [83, 85].

4.2. Typical materials used in boilers

Materials used in boiler pressure parts are performed in tubes and pipes, plate, forgings and castings. But vast majority of pressure parts demanded to bear high stresses, to resist corrosive conditions and to carry water/steam flux are performed as tubes. Thus tubes are used in such pressure parts as water walls (evaporator), superheater, reheater and economizers. Headers and air preheater, which are also required to resist aggressive media, also can be made from tubes. And typical materials used for all these parts are: carbon steel, low alloy steel, high alloy steel and stainless steels. In addition, in some extra cases composite tubes and coating of the tubes are used. Finally, all modern tubing materials for boiler pressure parts are presented in Table 4.1 [1, 5, 15, 70, 71].

Table 4.1. Typical tubing types of steel used in boiler pressure parts construction [5, 15, 86-95, 97].

Standard EN/ASME	Grade EN	Grade ASME	Application	Max. T of use, °C*
10216-2/ SA 106	P235GH	A	Waterwalls, low temperature superheaters	510
10216-2/ SA 106, SA 210	P265GH	B/A1	Waterwalls, low temperature superheaters	510
10216-2/ SA 209	16Mo3	T1a	Waterwalls, superheaters	525
10216-2/ SA 213, SA 335	13CrMo4-5	T11/P11	Superheaters, headers, waterwalls	560
10216-2/ SA 213, SA 335	13CrMo4-5	T12/P12	Superheaters, headers, waterwalls	560
10216-2/ SA 213, SA 335	10CrMo9-10	T22/P22	Superheaters, headers, waterwalls	600
10216-2/ SA 213, SA 335	7CrWVMoNb9-6	T23/P23	Superheaters, headers, waterwalls	600
10216-2/ SA 213, SA 335	7CrMoVTiB10-10	T24/P24	Superheaters, headers, waterwalls	600
10216-5/ SA 213, SA 335	X10CrMoVNb9-1	T91/P91	High temperature superheaters and headers	620
10216-5/ SA 213, SA 335	X10CrWMoVNb9-2	T92/P92	High temperature superheaters and headers	650
10216-5/ SA 213, SA 335	X6CrNi18-10	TP 304/ TP 304H	High temperature superheaters	760
10216-5/ SA 213, SA 335	X6CrNiTi18-10	TP 321/ TP 321H	High temperature superheaters	760
10216-5/ SA 213, SA 335	X7CrNiNb18-10	TP 347/ TP 347H	High temperature superheaters	760
10216-5/ SA 213, SA 335	X5CrNiMo17-12-2/	TP 316/ TP 316H	High temperature superheaters	760
10216-5/ SA 213, SA 335	X1CrNi25-21/ X6CrNiNbN25-20	TP 310H/ TP 310HCbN	High temperature superheaters	815

*Typical maximum accepted temperatures in pressure parts for listed steels are: A, B/A1, T1a – 450 °C, T11/P11, T12/P12, T22/P22, T23/P23, T24/P24 – 580 °C, T91/P91, T92/P92 – 600 °C, TP 304/TP 304H, TP 321/TP 321H, TP 347/TP 347H, TP 316/TP 316H – 620 °C, TP 310H/TP 310HCbN – 670 °C.

4.2.1. Alloying elements

Plain grades of steel are not applicable in extremely corrosive high temperature and pressure parts of boiler. New grades are obtained in case to improve mechanical, physical and resistance properties of steels. Alloying elements introduced in plain carbon steel structure provide desirable properties of boiler steel. However, it should be noticed that alloying elements have a synergistic effect, which should be considered in design process of steel. Some typical alloying elements and their effects are listed below (Table 4.2).

Table 4.2. Effects of the alloying elements.

Element	Improve	Deteriorate
C	Strength, hardness	Corrosion resistance, toughness, ductility
Si	Chlorine resistance, strength, hardness	Alkalie resistance
Mn	Sulfur resistance, strength, hardeness, malleability	Toughness, ductility
N	Intergranullar corrosion resistance, strength	-
Cr	Corrosion resistance, strength, hardness, toughness	Creep strength
Mo	Corrosion resistance, high temperature strength, ductility	-
Ni	Corrosion and chlorine resistance, strength, toughness	Sulfur resistance
Co	Strength	Creep strength
Ti	Corrosion resistance, high temperature strength	-
Nb	Corrosion resistance, ambient and high temperature strength	-
W	Creep strength, high temperature hardness	-
V	Strength, hardness, toughness	-
Tl	Strength, hardness, toughness	-
Pb	Machinability	-
Al	Chlorine and oxygen resistance	Creep strength
B	Hardness	-

Carbon (C) is the most common alloying element in steel. Essentially steel is a mixture of iron and carbon. Addition of carbon causes increase of strength and hardness and at the same time decrease of ductility and toughness of steel. Moreover high carbon content affects negatively on machinability, weldability, corrosion resistance but improves wear resistance. Finally, varying of carbon content changes physical properties (thermal, electrical conductivities and etc.) [5, 72, 73, 77, 82].

Silicon (Si) is the main deoxidizer and degasifier of steel. Typically has a moderate effect on steel's strength and hardness, but is not used as a strengthener. Steel with amount of silicon exceeding 2.5 % becomes brittle and loses ductility. Also, silicon is added to enhance electrical properties (electrical conductivity, etc.). Furthermore, silica (remains after deoxidation) protects steel against chlorine corrosion, but make it susceptible to alkali metals [5, 73, 77, 82].

Manganese (Mn) eliminates formation of iron sulfides and assists in deoxidation of the steel. Additions of manganese increase strength and hardenablility of the steel but in lower degree than carbon. Nevertheless provides strengthening effect as chromium does and better than nickel. In the same time, manganese decreases toughness, ductility and weldability but produce malleability essential for steels [5, 73, 77, 82].

Nitrogen (N) is interstitial strengthener of steel like a carbon, with the same degree. However in contrast with carbon it does not cause a corrosive effect and furthermore nitrogen is one of the main alloying elements which gives excellent intergranular corrosion resistance of stainless steel [5, 73, 80].

Chromium (Cr) is an important alloying element in stainless steels providing a protective oxide layer. Being not so strong oxide former, however, is very soluble in iron thus fully covers the steel by dense oxide film giving high temperature strength. Additions of chromium increase strength, hardness and toughness, but high chromium content makes steel sensitive to creep rupture. Moreover it improves hardenability and wear resistance. Finally, chromium alloying reduces thermal and electrical conductivity [5, 73, 77, 82].

Molybdenum (Mo) increases high temperature strength and minimizes embrittlement of steel at elevated temperatures. Moreover has strong hardenability and wear resistance improver. At the same time molybdenum is one of the main corrosion protective elements, which increases passivity of oxide film and has a tendency to reduce pitting corrosion of the steel [5, 73, 77, 82].

Nickel (Ni) being good austenite stabilizer is an important element for austenitic stainless steel. It increases toughness and strength without looses of ductility. Moreover improves impact and creep strength especially with chromium. Furthermore, in amounts more than 5 % nickel improves corrosion resistance properties of steel even at high temperatures. Nickel is a good agent against chlorine corrosion, but gives low protection against sulfur. Finally, it reduces thermal and electrical conductivity of the steel [5, 73, 77, 82].

Additions of chromium, molybdenum and nickel provide desirable properties of the steel, especially in high pressure and elevated temperature application. But each of them is very expensive. Thus increasing in content of any of these elements rapidly raises cost of the steel, which should be taken into account in material selection stage.

Cobalt (Co) suppresses hardenability, increase creep strength of the steel. Additions of cobalt highly improve strength of austenitic steel - in the greater degree than nickel does [5, 72].

Titanium (Ti) is a good deoxidizer and denitrider. It improves high temperature properties of the steel. Also, titanium increases corrosion resistance of stainless steels by reacting with carbon instead of chromium, thus keeping chromium on required level, Moreover it acts as carbide stabilizer in stainless steels [5, 73, 77].

Niobium (Nb) is used in small additions as stabilizer of carbides in stainless steels. Also increases strength and hardenability, but high niobium content causes decreases of hardenability. Moreover, like titanium it improves high temperature properties and corrosion resistance of the steel [5, 73, 77, 82].

Tungsten (W) is strong steel strengthener and forms carbides resistant to abrasion, which provide high temperature hardness. Also it improves creep strength of the steel [5, 73].

Vanadium (V) is used to increase strength, toughness, hardness and wear resistance of the steel. Also stabilizes structure at high temperatures and improves properties of other alloying elements. More rarely it is used as deoxidizer and degasifier of the steel due to high cost [5, 73, 77, 82].

Tantalum (Tl) usually is added as carbide stabilizer in stainless steels and cause properties similar to that which niobium does [73, 77].

Lead (Pb) is used to increase machinability of steels by lubrication and easier chip formation. Also it can cause liquid metal embrittlement due to low melting point [73, 74, 77].

Aluminium (Al) is an efficient deoxidizer. Aluminium forms dense oxide film and thus it is effective in oxidation protection. Although it does not increase protection against ordinary corrosion it is good against chlorine pitting corrosion, but expensive. High content of aluminium cause decrease of creep resistance [5, 77].

Boron (B) is the strongest hardener of steel even small amount can provide considerable effect [5, 73, 77].

4.2.2. Residual elements

Elements that come in steel making process with raw materials (basically scrap) and remain in steel due to difficulty of refining are called residual elements. Thus, residual elements unlike alloying elements are present in steel by default and cannot be removed completely. The main residual elements and properties, which they add to steel, are given below (Table 4.3).

Table 4.3. Effects of the residual elements.

Element	Improve	Deteriorate
P	Atmospheric corrosion, strength, hardness, toughness	Acid corrosion, ductility
S	Machinability	Ductility
Cu	Atmospheric corrosion, acid protection, strength	Sulfur resistanse
H	-	Strength, ductility
O	Strength	Fatigue resistanse, toughness, ductility

Phosphorus (P) presence increase strength, hardness and ductility of the steel, but in the same time cause embrittlement and loss of ductility. Also it is added in carbon steel to provide machinabaility. Finally phosphorous is considered to improve atmospheric corrosion resistance, but accelerate corrosion in presence of some acids [5, 73, 77, 82].

Sulfur (S) residuals decrease ductility and weldability and in the same time cause brittleness of the steel. Sometimes as a phosphorous it is added to improve machinability [5, 73, 77, 82].

Copper (Cu) in small amounts provides resistance against atmospheric corrosion and gives protection in reducing acids. Like nickel it is sensible to sulfur at high temperatures, but in high alloy steels provides corrosion resistance to sulfuric acid. Also it improves yield strength of the steel and increase strength and hardening after ageing [5, 73, 77].

Hydrogen (H) is undesirable residual in the steel. When it dissolves in steel structure it accumulates manganese sulfides and cause internal cracking similar to embrittlement [73, 74].

Oxygen (O) residuals form oxide inclusions which decrease ductility, toughness and fatigue resistance but slightly increase strength of the steel [5, 74].

4.2.3. Carbon steel

Carbon steels contain up to ~1 % carbon (typically carbon content is up to 0.2 % for carbon steels used in pressure parts), 1.65 % manganese, 0.60 % silicon, 0.60 % copper and residuals elements: the most common sulfur (0.05 % maximum) and phosphorus (0.04 % maximum) [72-75]. Other residual elements influence on steel properties less than sulfur and phosphorous. Thus limitations of these elements for steels are optional or eliminated [74].

European standard EN 10020 [76] define non alloy (carbon) steels by boundary values of alloying elements content (Table 4.4). Steel with chemical composition, where none of values in Table 4.4 is reached belongs to carbon steel grade.

Table 4.4. Boundary between non carbon and alloy steels (ladle analysis) [76].

Specified element		Limit value, wt%
Al	Aluminium	0.30
B	Boron	0.0008
Bi	Bismuth	0.10
Co	Cobalt	0.30
Cr	Chromium	0.30
Cu	Copper	0.40
La	Lanthanides (each)	0.10
Mn	Manganese	1.65
Mo	Molybdenum	0.08
Nb	Niobium	0.06
Ni	Nickel	0.30
Pb	Lead	0.40
Se	Selenium	0.10

Si	Silicon	0.60
Te	Tellurium	0.10
Ti	Titanium	0.05
V	Vanadium	0.10
W	Tungsten	0.30
Zr	Zirconium	0.05
Others (except carbon, phosphorus, sulphur, nitrogen) (each)		0.10

Mechanical properties of carbon steel primarily depend on carbon content. Low carbon steels used for pressure parts have low strength, high ductility thus they are malleable but cannot be hardened by heat treatment. However due to low content of carbon these type of steels have good weldability and do not have embrittlement in a weld joint. Moreover mechanical properties of carbon steel change steadily in a range of temperatures. Thus, tensile and yield strength of carbon steel decrease with temperature elevation [72, 82].

Oxidation of carbon steel is a common process giving corrosion resistance. But continuous growth of oxide layer can cause higher tube temperature and as a result failure due to insulating properties of scale. Nevertheless, carbon steels such P235GH and P265GH (see Table 4.1) with low carbon content are widely used in pressure parts (especially low pressure parts) of the boiler [5, 82].

4.2.4. Alloy steel

EN 10020 states lower limit of alloy steel shown in Table 4.4. If at least one of the limit values is reached than steel is considered to be alloyed. And it is left to be alloyed up to 10.5 % of chromium content, which is the minimum condition of stainless steel due to EN 10020 [76].

4.2.4.1. Low alloy steel

Low alloy steel is a subdivision of alloy steel. The exact definition value of low alloy steel is given in EN 10027-1:2005 as 5 % by weight of any alloying element. It means that if a content of every alloying element on average is lower than 5 % the steel belongs to low alloy grade [72, 78].

The main advantage of low alloy steels comparing to carbon steels is increased hardenability. Thus tensile strength of chosen low alloy steel can be twice higher than for carbon steel with the same carbon content. This fact can be explained by presence of alloying elements such as nickel, chromium and molybdenum. The alloying elements form finely divided carbides of treated steel increasing mechanical properties of alloy. Anyway, mechanical properties of low alloy steels considerably depend on content of carbon and like plain carbon steel, low alloy steel tend to form oxide scale. Ultimately 16Mo3 (T1a), 13CrMo4-5 (T11/P11, T12/P12), 10CrMo9-10 (T22/P22), 7CrWVMoNb9-6 (T23/P23), 7CrMoVTiB10-10 (T24/P24) are common low alloy steels for boiler pressure parts [5, 72, 77].

4.2.4.2. High alloy steel

In group of alloy steels there is a border between the low alloy steel and the high alloy steel and according to EN 10027-1:2005 the border is defined as 5 % of alloying elements. In case of high alloy steel it means if the average content by weight of at least one alloying element becomes equal or exceeds value of 5 %, the grade of steel becomes high alloy [78].

4.2.4.3. Stainless steel

En 10020 defines stainless steels as steels with minimum 10.5 % content of chromium and maximum 1.2 % of carbon. And can be divided further by nickel content as: stainless steel with nickel content less than 2.5 % (ferritic, martensitic) and with nickel content grater or equal 2.5 % (austenitic, austenitic-ferritic). Also stainless steel can be grouped by main property: corrosion resisting, heat resisting and creep resisting [76]. Thus, in general stainless steels are the high alloy steels, but due to corrosion resisting properties occurring after some chemical composition limit, stainless steel allocated to its own group.

Well known oxidation resistance of stainless steels comes from the protective Cr_2O_3 layer forming on the material surface. This layer becomes a continuous film when the content of chromium exceeds 18 % and reduces the oxidation of the underlying material being a barrier for oxygen. The film also contains protective spinel $FeCr_2O_4$, but it less protective than Cr_2O_3 scale due to worse resistance against oxygen diffusion. Presence of nitrogen and molybdenum are also considered as the main factors in pitting (local) corrosion protection by expanding the passive protective layer of stainless steels [5, 79, 80, 81].

There are four types of stainless steel classified by their crystalline structure: austenitic, ferritic, martensitic, duplex (austenitc-ferritic). Each group can be specified by one basic composition which defines general purpose of given steel type. Other compositions are derived from the basic one to obtain specific properties. These derivatives are obtained by variations of alloying elements [72, 75].

4.2.4.3.1. Austenitic steel

Austenitic steel has excellent corrosion resistance, but it is less resistant to cyclic oxidation comparing to ferritic stainless steel. Temperature creep and tensile strength are higher comparing with carbon steels. Austenitic steel is highly formable and weldable. It can be soft with yield strength about 200 MPa and also can be made very strong with yield strength above 2000 MPa also extra strength is provided by cold processing. Austenitic steel can be used up to 670 °C (see Table 4.1) thus it has been used in superheaters and reheaters for 55 years [5, 77, 79, 80, 81].

Austenitic stainless steel contains at least 18 % of chromium and 8 % of nickel. However, chromium content can vary from 16 % up to 30 % and nickel from 8 % up to 35 %. These specific chromium and nickel content (comparing with other stainless steels) play role of stabilizer that maintains the austenitic structure of the alloy in all range of temperatures and gives known high corrosion resistance [5, 72, 77, 79, 80, 81].

The superior corrosion resistance of austenitic stainless steel among the other is caused by good solubility of nitrogen and high content of nickel. Source [80] shows that in high chromium stainless steels increase in nickel content leads to higher corrosion resistance. Unfortunately SCC is the weakest side of austenitic stainless steel, which commonly cause failure in high pressure parts of boiler. Nevertheless, increase of chromium, nickel and molybdenum content enhance resistance to SCC. Moreover, corrosion resistance is strongly depends on content of the chromium in the surface. Scaling of the austenitic steel decreases chromium content under oxide layer and causes sensitization. Thus mechanical or chemical treatment is provided to remove this scale and increase corrosion resistance to severe conditions [5, 78, 80, 81].

Therefore, due to listed properties of austenitic stainless steel it is commonly used in pressure parts of boiler such as superheaters and reheaters exposed to high temperatures and high corrosive conditions. Following austenitic steels are commercially used: X6CrNi18-10 (TP 304/304H), X6CrNiTi18-10 (TP 321/321H), X7CrNiNb18-10 (TP 347/347H), X5CrNiMo17-12-2 (TP 304/304H) and X1CrNi25-21/X6CrNiNbN25-20 (TP 310H/310HCbN) (see Table 4.1).

4.2.4.3.2. Ferritic stainless steel

Ferritic stainless steel combines corrosion and heat resistance with moderate mechanical properties High temperature strength is less than austenitic steel's one. Also, it is less ductile than austenitic steel due to effect of small ferrite grain size and can be hardened by cold working. Chromium content varies in a range of 10.5 % up to 30 %. Thus ferritic steel can divided in three groups: low (10.5 – 12 %), medium (16 – 19 %) and high (more than 25 %) chromium. But in any case it contains no more than 2.5 % of nickel due to save ferrite structure. [72, 73, 75, 77, 80, 81].

Ferritic stainless steel has high temperature oxidation resistance up to 650 °C, but it less corrosion resistive than austenitic steel. Reduced pitting corrosion resistance comparing to austenitic steel is mainly caused by insolubility of nitrogen in ferrite and additionally by low content of nickel comparing with austenitic. Finally, structure of ferritic steel affects on decrease of corrosion resistance causing rapid reduction of local content of chromium in some cases [77, 80, 81].

Ferritic stainless steel has high resistance to SCC even in conditions causing pitting corrosion due to less susceptibility to hydrogen embrittlement. Moreover, reduced difference in thermal expansion of bulk metal and oxide film of ferritic steel makes it more applicable for cyclic high temperature applications [80, 81].

Despite the problems in application to heavy sections, especially with welding, caused by low temperature brittleness of manufactured grades, the ferritic steel is attractive by lower cost. Although stainless ferritic steels are not applicable in boiler construction, high strength alloyed ferritic steel grades X10CrMoVNb9-1 (T91/P91) and X10CrWMoVNb9-2 (T92/P92) (see Table 4.1) are used in typical boiler design [5, 80, 81].

4.2.5. Composite tubes

Composite tubes are needed when single material cannot withstand severe outside and inside conditions. Thus composite tubes consist of load carrying clad alloy and corrosion resistant core alloy. In addition, these two parts are metallurgically bonded in order to keep heat transfer properties. Typical combinations of bimetallic tubes core and clad alloys used for water walls, superheaters and reheaters are shown in Table 4.5 [5, 96].

Table 4.5. Typical alloys used in composite tubes [5, 96].

Trade grade	ASME grade	EN grade
Clad alloy		
Sandvik 3R12	304L	X5CrNi18-10/ X2CrNi19-11
Sandvik 3RE28	310	X5CrNiMo17-12-2/ X2CrNiMo17-12-2
Sanicro 28		X1NiCrMoCu31-27-4
Sanicro 38	Alloy 825 type	
Sanicro 63	Alloy 625 type	
Core alloy		
4L7	SA210-A1	P265GH
3Mo1	T1	16Mo3
HT5	T12	13CrMo4-5
HT8	T22	10CrMo9-10
HT7	T91	X10CrMoVNb9-1

4.2.6. Thermal coating

The thermal coating implies extremely thin protection layer compare even to composite tube clad layer which leads to saving of valuable material and decreasing cost of the product. Nowadays the range of offered coatings and methods of their spraying are developed enough to give desirable protection for different materials and meet any demand of the customer. The main advantages of thermal coating are wide range scale of application, portability, possibility of process automation, abrasion and erosion resistance, ability to seal, simple maintenance [119].

Thermal coatings provide two means of corrosion protection of wrapped materials. First is known as metallic spray coating or metalizing. It gives cathodic protection to the bulk material acting as a soluble anode and in the same time prevents direct contact with the environment. That is why materials used in this case should be less noble than steel or covered alloy. And they are usually represented by aluminium, zinc and their alloys and also may include aluminuium-magnesium alloys with applicable corrosion potentials [120].

Another mean of protection is spraying of dense and low porosity layer of corrosion resistant material such as stainless steels, nickel-base alloys (e.g. Alloy 625), titanium and other metals. Such coating forms very thin (less than 0.1 μm) oxide scale on treated surface which suppresses corrosive reactions. But unlike cathodic protection any break in passive oxide scale leads to crevice or pitting corrosion due to induce of anodic potential on protected material [5, 120].

4.3. Promising metals and alloys

Since biomass and waste utilization provides environment extremely corrosive for the materials applied in boiler combustion environment. The overview of already used and possible for utilization non ferrous metals and alloys is needed to be done. All presented materials are competitive to typical ferrous alloys (steels) due to their higher corrosion resistant properties accompanied by good mechanical properties which finally give effective price to life time ratio.

4.3.1. Duplex steel

Duplex steel is a mixture of austenite and ferrite structure desirably in equal amounts, which gives higher strength due to formation of austenite islands in highly alloyed matrix of ferrite which gives SCC protection. It has at least 20 % up to 26 % of chromium and low nickel content 4 – 8 % which makes it cheaper than the austenitic steel with the same corrosion resistant properties. Moreover, its greater strength requires less material and can replace of X2CrNiMo17-12-2 (316L) in the future. Although duplex steel is considered as highly corrosion resistant, but due to embrittlement is not applicable at temperatures above 300 °C [5, 77, 80, 81].

Duplex steel has excellent strength, toughness (between that of ferritic and austenitc steels), ductility (lower than austenitic) and corrosion resistance (like austenitic). Thus, it shows double yield strength with the same corrosion resistance level comparing with corresponding austenitic steels. Due to specific structure duplex steel has exceptional SCC (better than austenitic), fatigue resistance and has an advantage in aggressive environments (sulfuric, hydrochloric, phosphoric and organic acids, sodium hydroxide). Following grades of duplex steel should be taken into consideration: 2205, 2507, 2304 [5, 80, 81].

4.3.2. Maretensitic steel

Martensitic steel is a ferritic one in the annealed condition, but becomes martensitic after rapid cooling above some critical temperature. It is less machinable and weldable than austenitic and ferritic steels and can be hardened by tempering and quenching. Martensitic steel is resistant to corrosion just in mild conditions not in severe because it less alloyed due to keeping of martensite structure. Usually chromium content is in the range from 10.5 up to 14% (specific types contain 16-18 % of chromium). Also, martensitic steel can contain some nickel (less than 2.5 %) in order to increase corrosion resistance and toughness. Finally, it is least corrosion resistant from all of the stainless steels, susceptible to SCC, which makes it applicable just in mild environment up to 650 °C. One of the promising martensitic steel is HCM12 (12Cr-1Mo-1WVNb) [5, 72, 75, 77, 80].

4.3.3. Aluminium

Aluminium is very light metal with density of 2.7×10^3 kg/m^3. It has very good corrosion resistance, fabricable and relatively cheap material. In pure condition aluminium has very low strength but aluminium based alloys provide high strength to weight ratios. Resistance to corrosion appears with formation of thin (few atoms thick) but very protective oxide layer. Aluminium has high affinity to oxygen, so it rapidly reacts with oxygen, which provides self-healing properties [98, 99].

Aluminuim was widely used as a protection coating (see section 4.2.6.), but also aluminium and its alloys was used in power plants as slot wedges of generator rotors. Those application are represented by aluminium-copper alloys with 4 % of copper and small additions of magnesium and silicon [98].

One of the known aluminium alloys applicable to power plant construction contains 1 % of silicon and 0.5 % of magnesium belongs to 6xxx series (6063, 6005) and provides superior mechanical properties, slight reduction in weight and gives possibility to operate at higher temperatures. It shows good corrosion and SCC resistance properties and can find application in boiler heat exchangers tubing. This alloy treated by ageing has increased strength and hardness values and can be applied in winding wedges. Due to solidus temperature is 607 °C for 6005 and 615 °C for 6063 application of these alloys do not exceed 600 °C [99].

Also, source [99] presents some high-temperature aluminium-base powder metallurgy alloys with improved corrosion and SCC resistance. This list includes rapid-solidified aluminium-zinc-magnesium 7xxx series alloys 7091 and 7090, alloy 7064 with additions of zirconium, chromium and cobalt and alloy CW67 containing nickel and zirconium. Moreover, mechanically alloyed materials such as Al-9052 and Al-905XL with high strength with minimized corrosion and SCC susceptibility were developed.

4.3.4. Titanium

Titanium is known as low density (4.5×10^3 kg/m^3) and superior corrosion resistant material. Such a good resistance is provided by high reactivity (like aluminium has) which gives thin, hard and dense protective oxide film. Titanium does not corrode under conditions in which stainless steel and copper does. Also it is not susceptible to crevice and stress corrosion and erosion. From the water side of tubes titanium shows resistance to different salts and salty deposits. High-temperature titanium alloys can be used up to 595 °C, but titanium aluminides have a potential to be used in a range from 595 °C and up to 925 °C [98, 100, 102].

Titanium has two crystallographic forms – room temperature α phase and high temperature β phase with transition point at 883 °C. Thus, there are three types of titanium-base alloys: alpha alloys with, beta alloys and alpha plus beta alloys. Alpha alloys contain α phase stabilizing elements such as aluminium and tin and have good strength, toughness and weldability. Alpha alloys posse superior compare to beta alloys creep resistance which makes them preferable in high temperature applications [99].

Alpha plus beta alloys are α phase-base mixtures containing from 10 up to 50 % of β phase. The most known pattern of alpha plus beta alloys is Ti-6Al-4V alloy with good formability and properties of alloys based on this composition can be controlled by heat treatment. Beta alloys contain transitions elements such as vanadium, niobium and molybdenum which provide stabilization of β phase at temperatures lower than 883 °C. They have excellent hardenability and forgeability [99].

Although titanium products have good mechanical properties, low density and excellent corrosion, high cost limits their applications. Pure titanium such as Grade 2 manufactured by Sandvik is more used in corrosion resistant application than titanium based alloys. In energy industry applications titanium find its application in heat exchangers, condensers, tubing and piping which use see water as a coolant. In power generating sites titanium has been using as material for turbine blades and commonly used as static and rotating gas turbine engine components [98, 99, 101].

Nevertheless, such titanium-base alloys also manufactured by Sandvik as Grade 9 with 3 % of aluminium and 2.5 % of vanadium, low oxygen Grade 11 with additions of palladium, Grade 12 containing molybdenum and nickel have excellent oxidation and corrosion resistance and applicable to heat exchanger tubing and piping in power plant design. Relatively new applications for titanium alloys are in parts of scrubber units for treatment of coal fired power plants emissions and as tanks for low level radioactive waste fuel storing [99, 100, 101].

4.3.5. Zirconium

Zirconium is a ductile metal and have similar to titanium and austenitic stainless steel mechanical properties. It has corrosion resistance against many corrosive environments including superheated water. Such corrosion resistance appears due to formation of dense and stable oxide layer on metal surface which tends to self curing by continuous growth up to 550 °C. Therefore, zirconium is used as a fuel cladding in nuclear power plant reactors and some chemical-processing equipment experience severe corrosion conditions [100, 102].

Zirconium as titanium is an anisotropic material – it exhibit two allotropic forms with transition point at 870 °C. And the most commonly used zirconium-base alloys are consist of dilute α phase and have the same properties as pure zirconium. The main commercial grades of zirconium alloys - Zircaloys are Zircaloy-2 and Zircaloy-4 containing tin and oxygen as α phase stabilizers and also contain such stabilizers of β phase as iron, chromium and nickel Zircaloy-2 and -4 are used in nuclear service as a highly water and steam resistant alloys [100].

Other alloys of zirconium not belonging to Zircaloys are known. One of them containing niobium is Zr-2.5Nb, where niobium acts as a mild stabilizer of β phase. It has similar mechanical and physical properties as Zircaloys does but corrosion resistance is slightly reduced and used in pressure tubes of heavy water reactors. Another one non-zircaloy material is Zr-702 alloy provided by Sandvik which has immunity to SCC and high pitting and crevice corrosion resistance. It is used in such severe environments where high performance stainless steels could not survive [100, 101].

4.3.6. Copper

The strongest side of the copper is excellent electrical and thermal conductivity (second in conductivity list of pure metals). Also, copper is well formable and cold workable metal due to good ductility and malleability. Additionally, it has good corrosion resistance especially to air and water. Thus, coppers (> 99 % of copper) and dilute coppers (> 96 % of copper) such as phosphorous deoxidized copper (C12200) is applicable in evaporator and heat exchanger tubing [98, 99, 100].

Copper alloys have a big range of compositions which give different mechanical and corrosion resistance properties. However most of them are not applicable at temperature above 400 °C. The most common alloying elements provide following alloys: zinc – brasses, tin – bronzes, nickel – cupronickels and nickel silvers [98, 99, 100].

Brasses have composition of about 70 % of copper and up to 30 % of zinc. In this case zinc increase of ductility and provide optimum combination of strength, hardness and ductility for this alloy. However, brasses are susceptible for selective corrosion called dezincification, which replaces the original zinc in the alloy to porous copper. In addition, work hardened brasses are weak against SCC and brasses containing more than 15 % of zinc are the most susceptible to SCC. Arsenic aluminium brass (C68700) is applicable as evaporator and heat exchangers material [98, 99].

Most common commercial copper-tin bronzes are rarely used in power industry. But aluminium bronze with 5-6.5 % of aluminium content (C60800) can be used in evaporator and heat exchanger tubing [98, 99].

Cupronickels possess good toughness and machinability in combination with good corrosion resistance. Thus, alloy with 70 % of copper and 30% of nickel (C71500) has good corrosion resistance against sea water. But 90 % copper and 10 % nickel (C70600) alloys have better resistance to exfoliation. Cupronickels have high resistance to SCC and find application in water walls, economizers and heat exchanger tubes replacing mild steels [98, 99].

4.3.7. Nickel

Nickel has good strength and excellent corrosion resistance properties. This combination provides range of pure nickels and nickel-base alloys with high strength and corrosion resistance applicable at high temperatures. Nickel-base alloys are defined as alloys containing more than 30 % of nickel and all of them have an austenitic structure. They include: nickel-copper (Monels), nickel-molybdenum, nickel-chromium and nickel-chromium-iron (Inconels), iron-nickel-chromium (Incoloys) and iron-chromium-nickel (austenitic stainless steels) (Figure 4.1) [98, 100, 103].

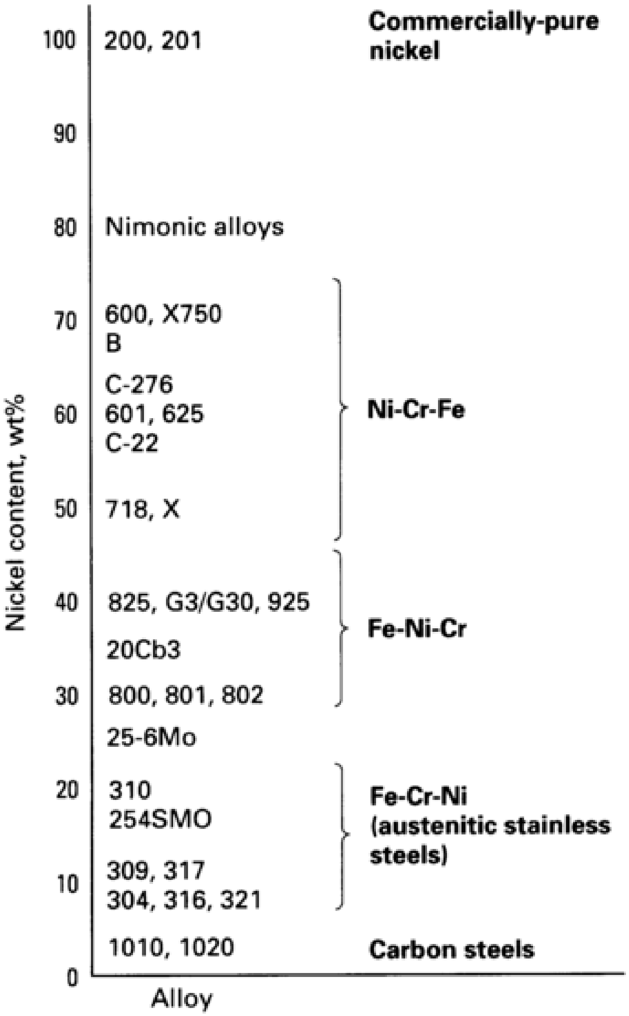

Figure 4.1. Chart ranging nickel-base alloys due to their nickel content [100].

Commercially pure nickel alloys 200-205 are known as highly resistant to many corrosive, especially reducing, environments. However, they are also used in oxidizing media supplying protective oxide surface layer. All of them are widely used in chemical-processing applications at low temperatures (Nickel 200 < 315 °C, Nickel 201 < 295 °C) due to embrittlement by graphite phase precipitation. But it is worth to be mentioned that Nickel 200 and 201 are used to handle concentrated caustic soda and dry chlorine [100, 103].

Low-alloy nickel alloys contain at least 94 % of base metal and represented by Nickel 211, Duranickel alloy 301 and Alloy 360. Thus, Nickel 211 contain up to 5 % of manganese which gives it resistant against sulfur. Duranickel 301 contains 4.5 % of aluminium and 0.6 % of titanium and possesses enhanced strength. Precipitation hardened Alloy 360 uses up to 2 % additions of beryllium and up to 0.5 % of titanium [103].

Corrosion resistant nickel-copper alloys are called Monels and contain up to 67 % of nickel and up to 33 % of copper with considerable levels of iron and manganese. Alloy 400, R-405 and K-500 are the most useful Monels due to their excellent formability and strength and also provides good general and chlorine corrosion resistance. Such properties allow using these alloys for handling of organic acids, caustic and dry chlorine and make them applicable in feedheater and condenser tubes in power plant design [98, 100].

Nickel-molybdenum alloys such as the latest corrosion resistant Hastelloy B 3 and B 4 (Nicrofer 6628). These alloys contain about 28 % molybdenum with 0.8-1.5 % additions of iron and chromium up to 1.5 %. B 3 and B 4 possess superior thermal stability and excellent corrosion resistance against hydrochloric acid and different reducing environments [103].

Inconels are nickel-chromium and nickel-chromium-iron composition alloys with high temperature application up to 1200 °C and outstanding temperature strength up to 540 °C. Common representatives of corrosion resistant nickel-chromium-iron alloys are Inconel Alloys 625, G3/G30, C 22, C 276, 690 which basically contain from 15 % to 30 % of chromium and 3 % to 20 % of iron, where the balance is nickel. These alloys show good formability and high temperature strength, they are excellent in pitting, intergranular and chlorine corrosion resistance and thus they are preferred for steam generator tubing [5, 98, 100, 103]. In source [98] 50 nickel 50 chromium alloy (50Cr-50Ni-Nb) is mentioned as an applicable material for superheater and reheater tubing. It contains nominal amounts of nickel and chromium which gives excellent high temperature oxidation and corrosion resistance.

Iron-nickel-chromium alloys are known as Incoloys and usually have minimum 37 % of iron and 19-29 % of chromium with small addition of aluminium and titanium (0.15-0.60 % each). Commercially important Incoloy Alloys 800, 800H, 800HT, 801, 802, 825 and 925 find high temperature application up to 1150 °C and show good oxidation resistance, resistance to chloride-ion CCS. And as Inconels they possess high temperature strength that is why Alloys 625 and 825 are used as typical material for outer corrosion resistant layer of composite tubes (see Table 4.5). Also, all listed Incoloys are commonly used in catalytic cracking and reformer tubes [100, 103].

Equiatomic nickel titanium alloy is known as material with structure memory. Usually it returns intial shape after being deformed at lower temperatures. This self repair function makes it useful in condenser and economizer tubes. Application in hotter parts is impossible due to creep cracking above 350 °C [98].

4.3.8. Cobalt

Cobalt is heavy and tough metal with high chemical reactivity (higher than nickel one). It has good corrosion, wear resistance and high temperature strength which provide three main types of cobalt-base alloys: heat resistant, corrosion resistant and wear resistant alloys [100, 103].

High temperature alloys use additions of tungsten, molybdenum, moderate nickel, low carbon and rare-earth metals which provide high temperature strength, thermal and oxidation resistance. Typical commercial alloys are: Haynes Alloys 25 (L605) and 188, MAR-M Alloy 509. Common high temperature application of these alloys is within gas turbine industry. Alloy 509 is used for complex shapes products such as nozzles of gas vanes. Alloy 188 is used in combustor cans and afterburner liners of high performance aircraft gas turbines. Alloy 25 has been used in construction of industrial furnaces. They excellently withstand sulfidation coupled with burning low-grade fuel including waste at modern power plants [100, 103].

Corrosion resistant alloys Haynes Alloy 1233 and Alloys MP159 and MP35N (multiphase alloy) have excellent resistance to aqueous corrosion. Their resistance is based on chromium and molybdenum content, Alloy 1233 additionally contains tungsten. Alloy 1233 alloy is excellent against pitting and crevice corrosion and has excellent erosion resistance. MP159 and MP35N alloys show ultrahigh strength, high ductility, corrosion resistance especially in mineral acids and chloride solutions and high resistance to SCC. Finally, cobalt-base alloys are less resistant to CSS than nickel-base alloys, but considerably better in CSS than stainless steels [100, 103].

Wear resistant cobalt-base alloys are predominantly represented by Stellites. There are six common wear resistant alloys: Stellite Alloys 1, 6, 6B, 12, 21 and Tribaloy alloy (T 800). Alloys 1, 6 and 12 are based on cobalt-chromium-tungsten structure with some carbon content. Here Alloy 1 is the hardest, most abrasion resistant and lest ductile. These common wear resistant is described by precipitation of chromium rich M_7C_3 and tungsten-rich M_6C carbides. Alloy 21 additionally contains molybdenum as solution strengthener and less carbon, which makes it more resistant to corrosion than previous three alloys. Alloy 6B differs from previous four by that he is used as wrought products, which gives enhanced ductility, chemical homogeneity and abrasion resistance. Finally, Alloy T 800 is highly alloyed by molybdenum and silicon in order to induce formation of intermetallic phase which provides outstanding abrasion resistant but limits ductility. Cause of this ductility limitation has forced to use of T 800 as plasma-sprayed coatings [100, 103].

Additionally, cobalt is widely used as a component of nickel-base superalloys in a range of 10-15 wt%. Where it acts as solid-solution strengthener and lowers the solubility of aluminium and titanium. Also, it reduces inter granular corrosion risk of nickel-base superalloys by inhibiting of precipitation of carbides and thus depletion of chromium at the grain boundaries [100, 103].

4.3.9. Chromium

Chromium is extremely hard metal, resistant to oxidation and inert in nitric acid, but can be dissolved by sulfuric and hydrochloric acids. And at temperatures above 816 °C it is susceptible to intergranular corrosion. Pure chromium has been used as a protective deposition coating for boiler components and this process is known as chromizing similar to thermal coating (see section 4.2.6.). Typically, chromium is not used in chromium-base alloys, but finds application in stainless steels, heat resistant alloys, high strength alloys, wear resistant alloys and electrical resistance alloys (see sections 4.2.4., 4.3.1, 4.3.2., 4.3.7. and 4.3.8.) [5, 72].

4.3.10. Molybdenum

Molybdenum is ductile and thus has good machinability and its mechanical properties strongly depend on purity of the metal. It has relatively high tensile strength and outstanding heat and electrical conductivity. At temperatures above 760 °C molybdenum forms oxides that evaporate after the formation, nevertheless it has high corrosion resistance and can be used at temperatures up to 1649 °C. Commonly it is used in steels, heat and corrosion resistant alloys (see sections 4.2.4, 4.3.7. and 4.3.8.). Also, molybdenum-rhenium alloys with 5 and 41 % of rhenium are known to be used in thermocouples [72, 100, 102].

4.4. Conclusion

Due to tendency of stainless steels and non ferrous alloys with additions of nickel, cobalt, chromium and molybdenum excellent resist to corrosion, it was decided to provide thermo balance tests with these metals (including Alloy 625) in pure condition in order to evaluate their personal resistant properties against oxidation in presence of chlorine containing deposit.

5. THERMAL BALANCE TESTS

5.1. Thermal Analysis

Thermal analysis (TA) is a type of analysis which defines properties of investigated a sample in a relation to its temperature variation. Properties that can be measured are thermodynamic properties (mass, volume, heat, etc.), material properties (hardness, Young's module, etc.), chemical composition and structure. Temperature alteration can be predetermined (programmed) or sample-controlled. In general, the sample being heated in equipment's furnace sends signals via detector to data processor placed in the computer unit, where temperature controller sets the values regarding to the chosen mode. Thus, any instrument for TA have the same block diagram as it was described above and is shown on Figure 5.1 [110, 111].

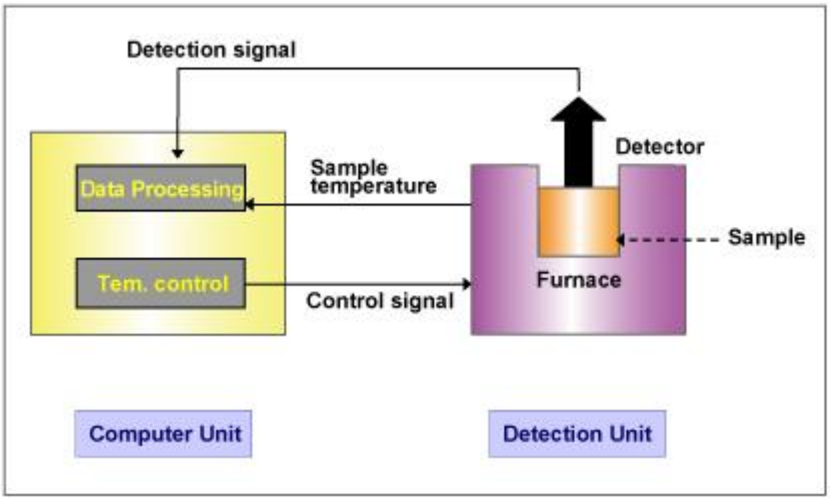

Figure 5.1. Block diagram of thermal analysis instrument [111].

Classical thermal analysis uses differential methods of measurement such as *differential thermal analysis* (DTA) and *differential scanning calorimetry* (DSC). Differential means that measured properties of the sample are compared simultaneously to properties of reference placed in the same conditions. Thus, the difference of obtained properties (temperature for DTA and heat flow rate for DSC) is the output and gives following advantages: differential signal can be amplified, which gives high sensitivity to the analysis; external factors compensate each other if they applied to both samples [110].

Thermogravimetry analysis (TGA) is a method of thermal analysis which detects the change in mass of investigated sample caused by evaporation, decomposition, oxidation and other processes in a relation to time or temperature. TGA is based on comprising of electronic microbalance of sample inside a furnace in couple with a temperature programmer and should be processed in closed system in order to obtain controllable atmosphere [110].

The simultaneous usage of DTA/DSC and TGA is called *simultaneous thermal analysis* (STA). It is the most useful way to identify thermal decomposition, oxidation, dehydration, heat resistance, kinetics analysis of the sample. STA allows defining behavior of the chosen material in a range of different atmospheres and temperatures by indicating lose or gain of mass followed by temperature or heat flux rate change.

5.2. Experiments

5.2.1. Equipment

Installation where the tests were conducted is consisted of *NETZSCH STA 449 C Jupiter* instrument and *NETZSCH QMS 403 C Aeolos - quadrupole mass spectrometer* (QMS) (Figure 5.2). Scheme of the *NETZSCH* device for STA is represented in Figure 5.3 and it is clear that there are two main parts: convectively heated attachable furnace module and built in balance system.

Figure 5.2. Laboratory installation for thermal balance tests.

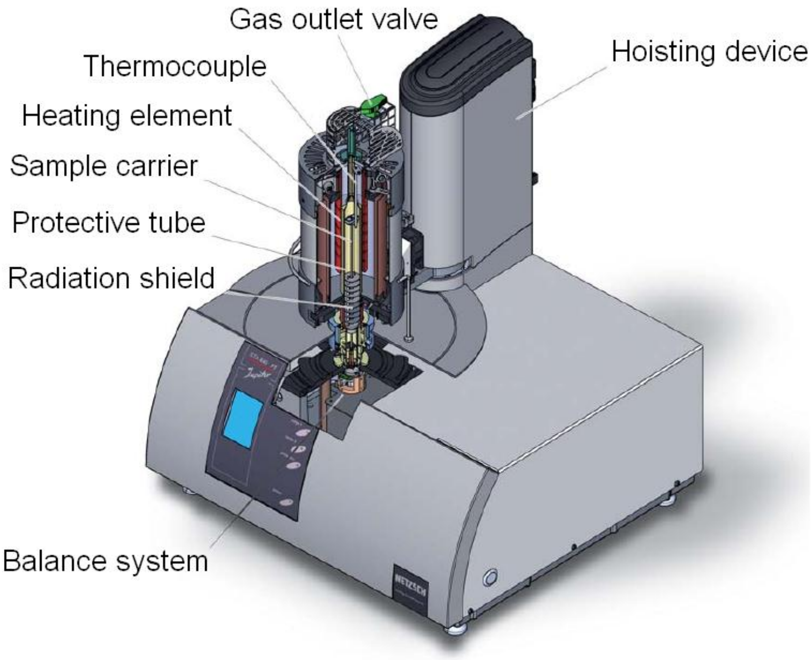

Figure 5.3. Structure of Netzsch STA instrument [112].

The sample is placed in top loading sample carrier which is installed inside protective tube covered by resistive heating element which rises the temperature of furnace surface and environment around the sample. Thermocouple is mounted inside the furnace in such a position (close to the sample) providing reliable temperature signal of the sample. For temperature below 800 °C the heating is defined by convective gas flow inside protective tube, but at higher temperatures radiate heating becomes dominant and samples should be protected by radiation shield. Finally, gas outlet valve is mounted in the furnace system in order to control the atmosphere inside the device. Thus, it could serve as a tool for obtaining vacuum environment, protective or purge gas atmosphere (see Figure 5.3) [110, 112].

The balance system provided by *NETZSCH* includes vertical single arm with electromagnetic compensation and represented by sensor element which consists of thermocouple and heat-flux plate sensor. This system has the same principal as common null point scaling but as a counterbalance uses current supplied to electromagnet to restore the balance [110].

The main idea of QMS is a filter which is represented by four bounded metal rods (Figure 5.4). Pairs of opposite rods are electrically coupled by different potentials and supply oscillating electric field. Detection of the sample ions is based on their mass to charge ratio which affects on stability of the ions trajectories inside the quadrupole filter [113,114].

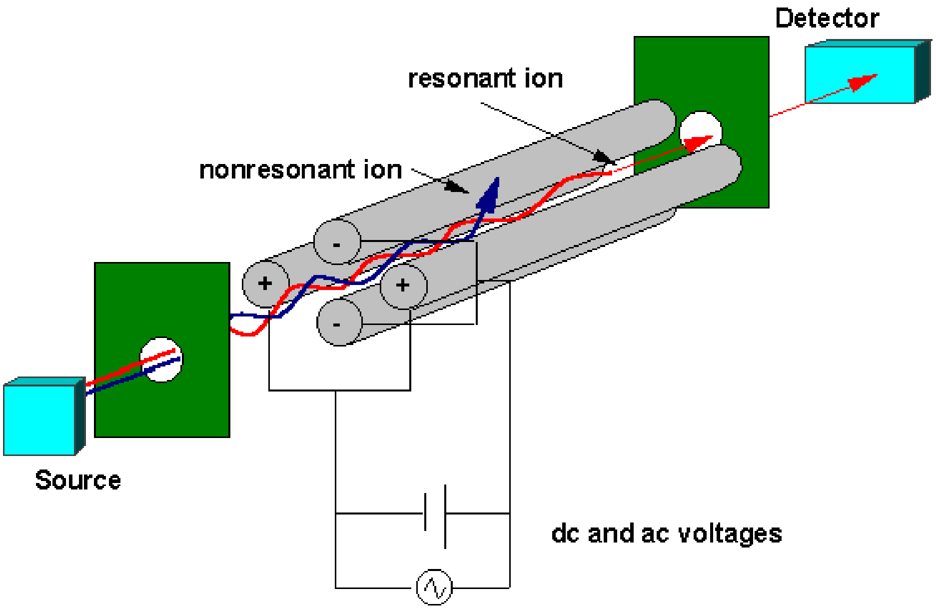

Figure 5.4. Schematic structure of quadrupole filter [113].

5.2.2. Methodology

Experiments were conducted regarding to previously planned matrix (Table 5.1). It consists of eleven cases but assumes thirteen tests due to replication of tests with cobalt – in order to evaluate reproducibility of cobalt. The first test out of thirteen is a reference for potassium chloride – sample of potassium chloride without an addition of any metal powder. During the tests potassium chloride modulates corrosive deposition of burned biomass on superheater/reheater surface.

Table 5.1. Thermal balance tests matrix.

Metal powder	Salt	Number of tests
-	KCl	1
Cr	-	1
Cr	KCl	1
Ni	-	1
Ni	KCl	1
Mo	-	1
Mo	KCl	1
Co	-	2
Co	KCl	2
Alloy 625	-	1
Alloy 625	KCl	1

The other twelve experiments represent testing of metals chosen in the end of chapter four (chromium, nickel, molybdenum, cobalt and alloy 625) as perspective materials for boiler tubes. Each metal is processed twice - as a single sample and as a mixture with potassium chloride except cobalt as it was mentioned above. Mixture of metal and salt in molar ratio 1:1 simulates deposit corrosion and a single metal test is a reference to non corrosive environment. Both of these cases should be compared in order to evaluate corrosion rate (metal loss or gain) and thus appliance of listed metals. Materials were chosen in that way (Table 5.2) to provide clear detection of mass and heat flow changes due to high contact surface between material and salt.

Table 5.2. Grain size of used materials, * - pro analysis.

Material	Grain size, μm
KCl	PA*
Cr	<150
Ni	<150
Mo	45-75
Co	<37
Alloy 625	45-90

Each thermal balance test was conducted in a range of temperatures 25-700 °C using temperature program. Thus, heating rate of the samples was 20 K/min inside 25-400 °C gap and 2 K/min for remaining temperatures (400-700 °C). In addition, atmosphere for temperature below 400 °C was inert and represented by helium flow 50 mL/min. At 400 °C the inert atmosphere was replaced by oxidative atmosphere consisted of synthetic air (80 % N_2 and 20 % O_2) flow 100 mL/min. These switch of atmosphere helps to study behavior of chosen metals inside temperature range of interest.

Preparing of the samples is consisted of scaling material powder in a range of 20-25 mg on micro scales and in case of salt-containing tests preliminary mixing. Then, samples were loaded in STA instrument crucibles made of alumina and calibration of the equipment is started. After calibration the temperature program was begun automatically and lasted till the end of measurement simultaneously with recording the output information such as DTA/DSC curves, TG curves, flows of gases formed during combustion.

5.3. Results and discussions

The results of STA are presented in Figures 1-22 - *APPENDIX 1*. The lately conducted test with empty crucible defines the baseline of the equipment. The empty crucible was treated by the same temperature program as the studied metal samples but with switching of injected air flow (50/100 mL/min – 100 mL/min) in order to understand reasons of endothermic effects and mass loss near 400 °C in Figure 1-22. This "gas injection" test showed that the empty crucible undergoes mass changes caused by change of flow and nature of the gas. Thus, corresponding corrections of initial data should be made in a way to eliminate mass change of "empty crucible" caused by change of gaseous flux rate. Mentioned corrections assume following changes: the results below 400 °C were cut, change in mass caused by flux of the gas were subtracted from initial data (Figures 3-22) and finally initial oxidation point of sample was taken as 100% of mass. The thermogravimetry curves of conducted tests with made corrections are presented in Figure 5.5 and 5.6.

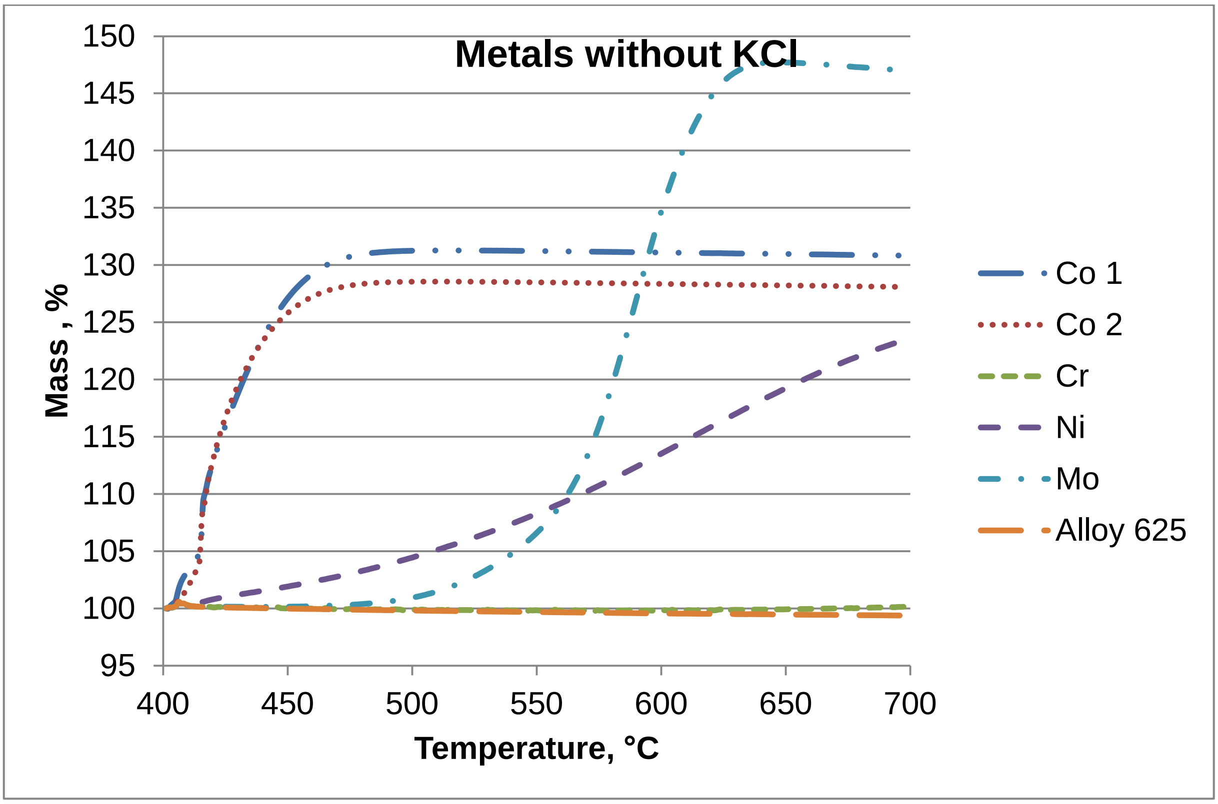

Figure 5.5. Thermogravimetric results for single metals.

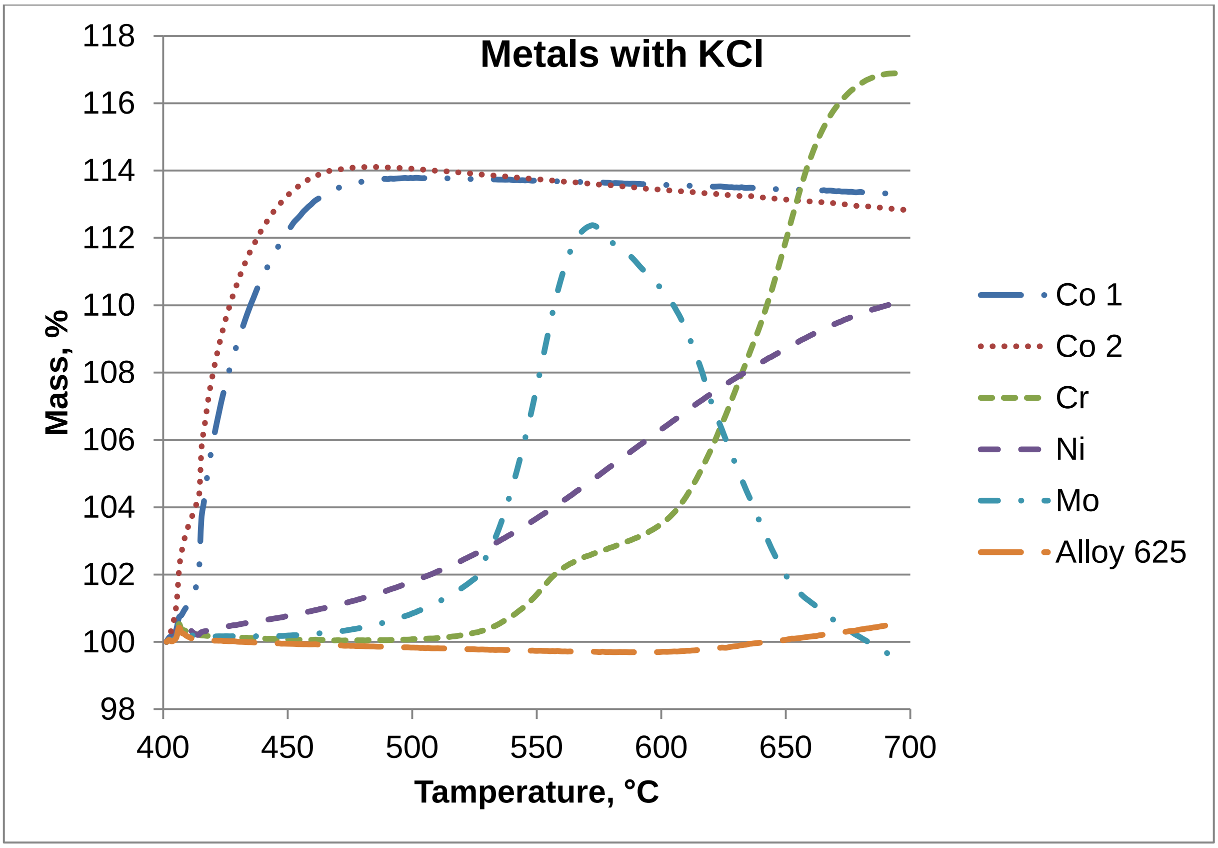

Figure 5.6. Thermogravimetric results for metals with potassium chloride.

Phase transition temperatures of chlorides of chosen metal are listed in Table 5.3. This table shows that formation of molten phase does not occur in studied temperature range (25-700 °C) except molybdenum chloride. Furthermore, forming molybdenum pentachloride has low boiling point – 268 °C (see Table 5.3) and undertakes decomposition on molybdenum tetrachloride and chlorine ($MoCl_4^+$ and Cl^-) above 268 °C [118]. Thus, it will form molybdenum tetrachloride since it begins to vaporize (see Figure 5.9). Vaporization of volatile chlorides of other metals is also possible (see Table 5.3) but due to relatively high partial pressure of oxygen within synthetic air (0.2 atm.) at scale-gas boundary they will be again oxidized eventually (see Figures 5.7, 5.8, 5.10).

Table 5.3. Melting points, temperatures of vapor pressure reaches 10^{-4} atm and boiling points of studied metal chlorides [117].

Metal	T_{melt}, °C	T at 10^{-4} atm, °C	T_{boil}, °C
$CoCl_2$	740	587	1025
$CrCl_2$	820	741	1300
$CrCl_3$	1150	611	945
$MoCl_5$	194	58	268
$NiCl_2$	1030	607	987
KCl	772	706	1407

5.3.1. Runs

Potassium chloride derived data shows that nothing happens with the sample in the whole range of temperatures (25-700 °C). There are no peaks of heat flow and no considerable mass changes (0.20 %) - just slight changes can be seen (Figure 1). Figure 5.7 shows that just slight oxidation of potassium chloride is possible.

Chromium undergoes just minor oxidation during the test which is clearly seen from slight gain of mass (1.32 %) and increase of heat flux (Figure 3). The formed oxide should be represented by chromium (III) oxide at applied experimental conditions (see Figure 5.7). Addition of potassium chloride leads to more rapid and deeper oxidation of chromium accompanied by two exothermic peaks and comparatively high total increase of mass (17.84 %) (Figure 5). These peaks represent beginning of oxidation at approximately 530 °C and more rapid further oxidation starting at around 600 °C. Single chromium shows slight character of oxidation rate (Figure 5.5) while presence of potassium chloride provide complete oxidation with achieving clearly identified limit (Figure 5.6).

Researches [115] and [116] confirm the oxidation of chromium to chromium (III) oxide in presence of potassium chloride. Where potassium chloride just takes role of catalyst and can form an intermediate potassium chromate (K_2CrO_4) compound – probably represented by the first peak appeared on Figure 5. Additionally, formation of potassium dichromate ($K_2Cr_2O_7$) as intermediate salt is suggested. Finally, there is evidence that obtained chromium oxide forms highly porous and non protective scale.

Nickel as chromium undergoes oxidation during the test with single metal sample but the rate of oxidation compare to chromium is higher (Figure 5.5). More rapid mass gain (24.38 %) can be seen coupled with gradual exothermic heat flow (Figure 7). Mixture with potassium chloride provides almost the same degree of nickel oxidation (Figure 5.11) – comparable to single sample gain of mass (11.20 %) and does not cause any rapid exothermic effects (Figure 9). Nevertheless, nickel oxide (NiO) is assumed as the main product in both cases (Figure 5.8).

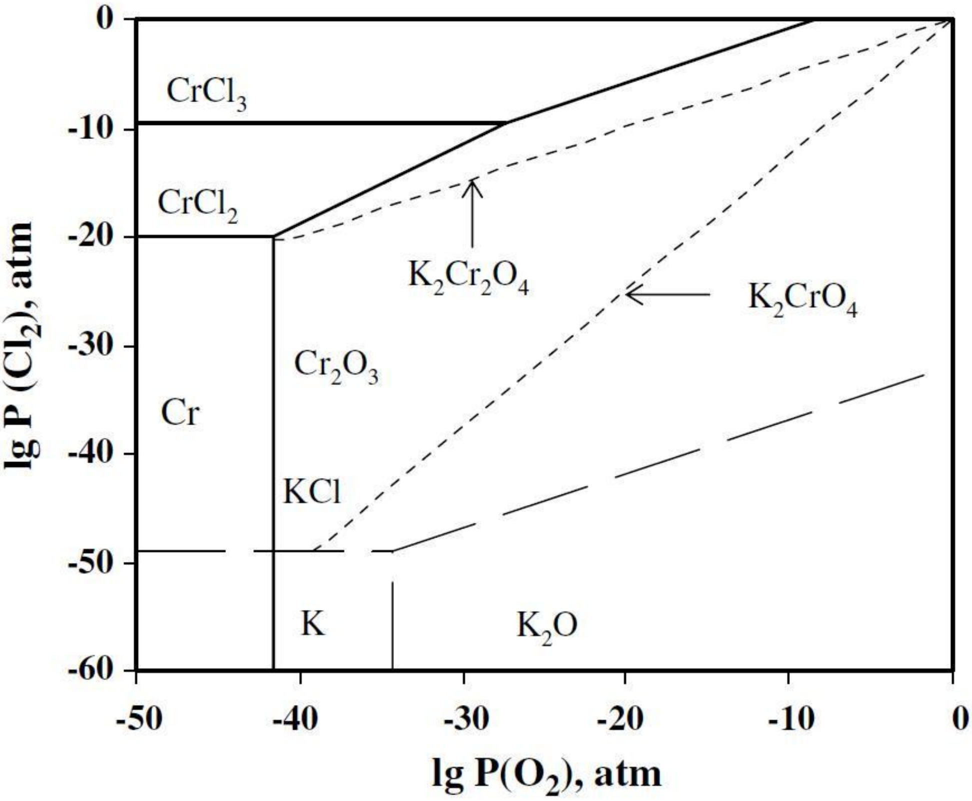

Figure 5.7. Thermodynamic stability diagram of K-Cr-O-Cl system at 500 °C [121]

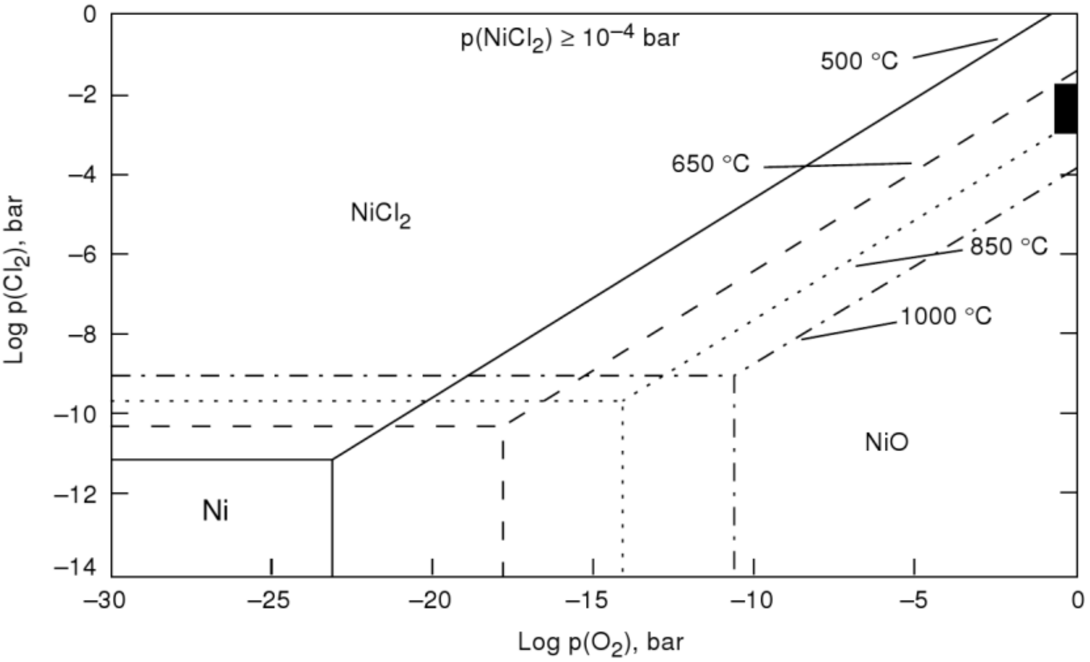

Figure 5.8. Thermodynamic stability diagram of Ni-O-Cl system in a range of 500-1000 °C [117].

Molybdenum runs have cardinally different picture. Again single metal undergoes severe oxidation with reaching of clearly detectible limit and provide huge gain of mass (47.77 %) compare to other tested materials (Figure 5.5). The mass gain is accompanied by clear and comparably high exothermic pick starting since injection of synthetic air at 400 °C (Figure 11). Furthermore, addition of potassium chloride, as it was claimed, changes the results. Thus, oxidation proceeds with simultaneous evaporation of volatile molybdenum chloride (Figure 13). Moreover, the change of TG curve slope accompanied by initial point of heat flow peak near 530 °C is a signal of rapid oxidation of molybdenum forming molybdenum trioxide (MoO_3) (Figure 5.9). And after complete oxidation (gain of mass is 12.97 %) of molybdenum at approximately 570 °C the mass of the sample begins to decrease with considerable rate reaching the initial mass of the sample. Detectable endothermic heat flow starting at 570 °C and slope change of DSC curve at 540 °C are a proof of volatilization of formed molybdenum chloride. Finally, partial adsorption of sample by crucible was suggested.

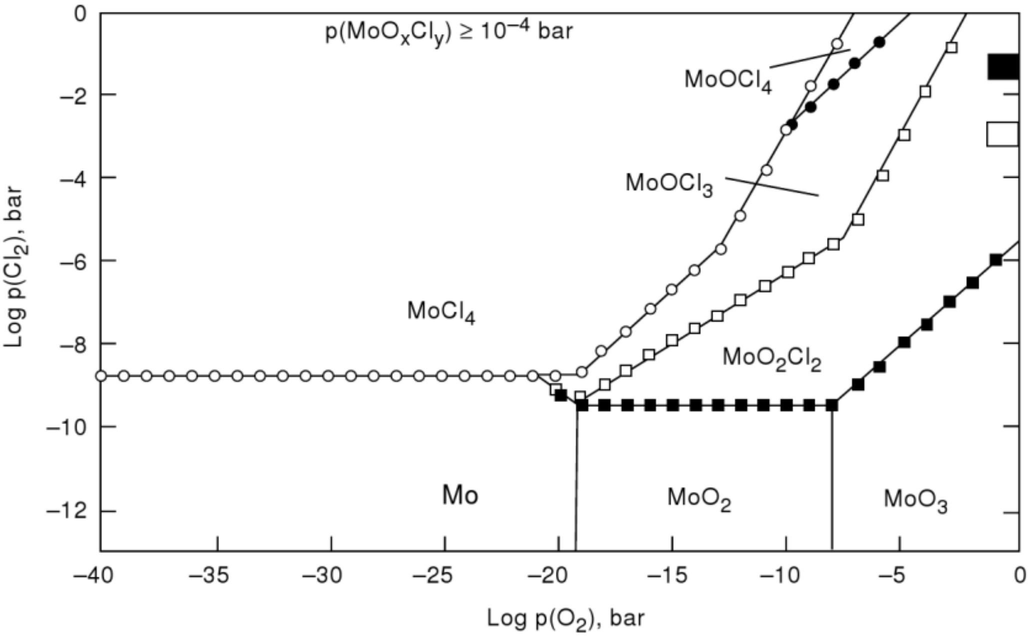

Figure 5.9. Thermodynamic stability diagram of Mo-O-Cl system at 800 °C [117].

Cobalt was tested twice and has shows reproducible results: in each case it has moderate mass gain (Figure 5.5). Since injection of synthetic air at 400 °C tested samples undergo rapid increase of mass coupled (28.47 % and 29.96 %) with clear narrow exothermic peak which ends at about 410 °C (Figure 15). Figure 5.10 shows that the only product which can be formed is cobalt (II, III) oxide (Co_3O_4 or $CoO{\cdot}Co_2O_3$) with mixed valence of cobalt. And as in case of nickel addition of potassium chloride does not give any difference – approximately the same mass increase (13.12 % and 11.64 %) in both cases (Figure 5.6). Moreover, rate of oxidation and even the same beginning and end of the exothermic effects (400 °C and 410 °C) are the same as for single metals (Figure 17). Furthermore, each sample of cobalt undergoes complete oxidation during the experiment with clearly defined limit value in Figure 5.5 and 5.6.

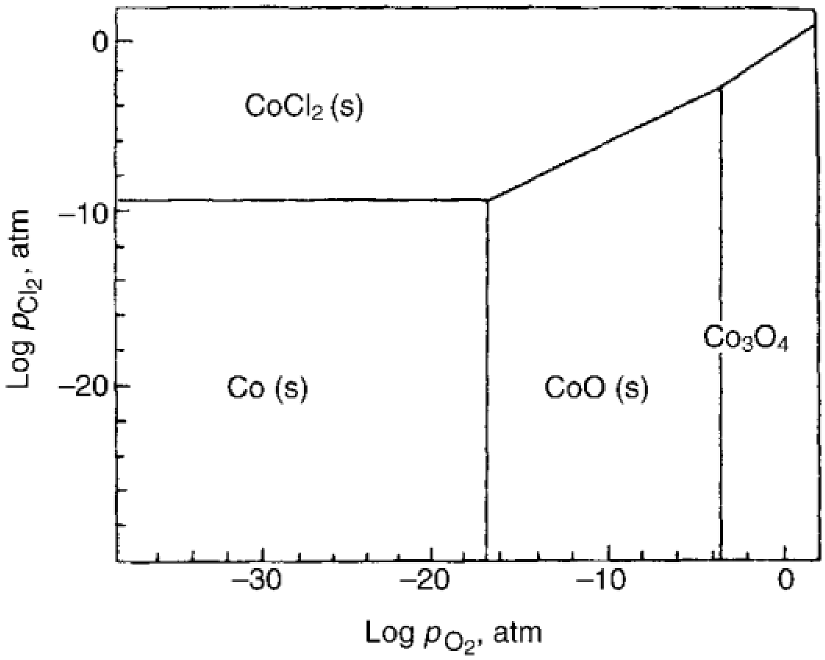

Figure 5.10. Thermodynamic stability diagram of Co-O-Cl system at 723 °C [117].

Alloy 625 is more complicated material which shows synergetic character of protective properties against oxidation and giving following results. Single sample of this material undergo slight oxidation which is followed by tiny mass gain (0.59 %) and steady gradual exothermic flow (Figure 19). Potassium chloride increases final mass of the sample (1.74 %) and as it can be seen near 600 °C the slope of curve is changed and oxidation become more rapid with corresponding bend of heat flow curve (Figure 21). Excellent oxidation and corrosion resistance of Alloy 625 compare to other metals can be seen in Figures 5.5 and 5.6.

5.3.2. Conclusions

In conclusion, relative oxidation of each sample except Alloy 625 was calculated for each 50 degrees in the range from 400 to 700 °C and presented in Table 5.4. Moreover, samples of cobalt showed their reproducibility (see Figure 5.5 and 5.6) and average value of oxidation was calculated (see Co_{av} in Table 5.4). In addition, oxidation of cobalt, chromium, nickel and molybdenum at 550 °C as a current industrial work temperature is visually represented in Figure 5.11. Finally, oxidation of Alloy 625 is difficult to calculate due to its complicated composition. Thereby, the resistance to corrosion of Alloy 625 is evaluated using TG results which are separately shown in Figure 5.12.

Table 5.4. Relative oxidation of studied samples, %.

Samples	Co_{av}	Co_{av}+KCl	Cr	Cr+KCl	Ni	Ni+KCl	Mo	Mo+KCl
450	72.64	78.72	0.08	0.40	6.98	6.29	0.30	0.67
500	81.94	85.79	-	0.43	16.20	14.72	1.86	3.01
550	81.83	84.59	-	7.44	30.16	30.15	13.16	27.02
600	81.46	83.29	-	18.31	49.26	51.82	68.96	36.90
650	81.07	81.95	-	62.43	70.07	71.49	94.57	-
700	80.73	80.46	0.32	87.99	85.40	83.17	93.13	-

Pure chromium has excellent resistance in the whole range of oxidation temperatures (400-700 °C) – 0.32 % of oxidation even at 700 °C. The intermediate oxidation is minor and difficult to measure since the corrections were applied to initially derived data. Potassium chloride accelerates the corrosion rate of chromium and cause 7.44 % of oxidation at 550 °C (Figure 5.11). Moreover, oxidation above 550 °C should be considered as possibility of future application of chromium as superheater material for higher temperatures. Thus, oxidation rate rises but not so crucial till 600 °C – 18.31 % and then increases significantly. Thereby, already at 650 °C the level of oxidation is 62.43 % and at 700 °C chromium completely oxidized – 87.99 %.

At the same time, nickel has different picture of oxidation. Samples of pure nickel and mixture with potassium chloride have almost the same rate of oxidation at studied temperatures (see Table 5.4). Thereby, the inertness of nickel to potassium chloride can be stated. Nevertheless, nickel has good resistance up to 500 °C with 14.72 % and 16.20 % oxidation with and without potassium chloride correspondingly. Cut at 550 °C shows 30.15% of oxidation which is about four times higher than in case of chromium (Figure 5.11). Then, nickel undergo steady oxidation without any increase even slight reduction in rate closer to 700 °C and gives 51.82, 71.49 and 83.17 % of oxidation at 600, 650 and 700 °C.

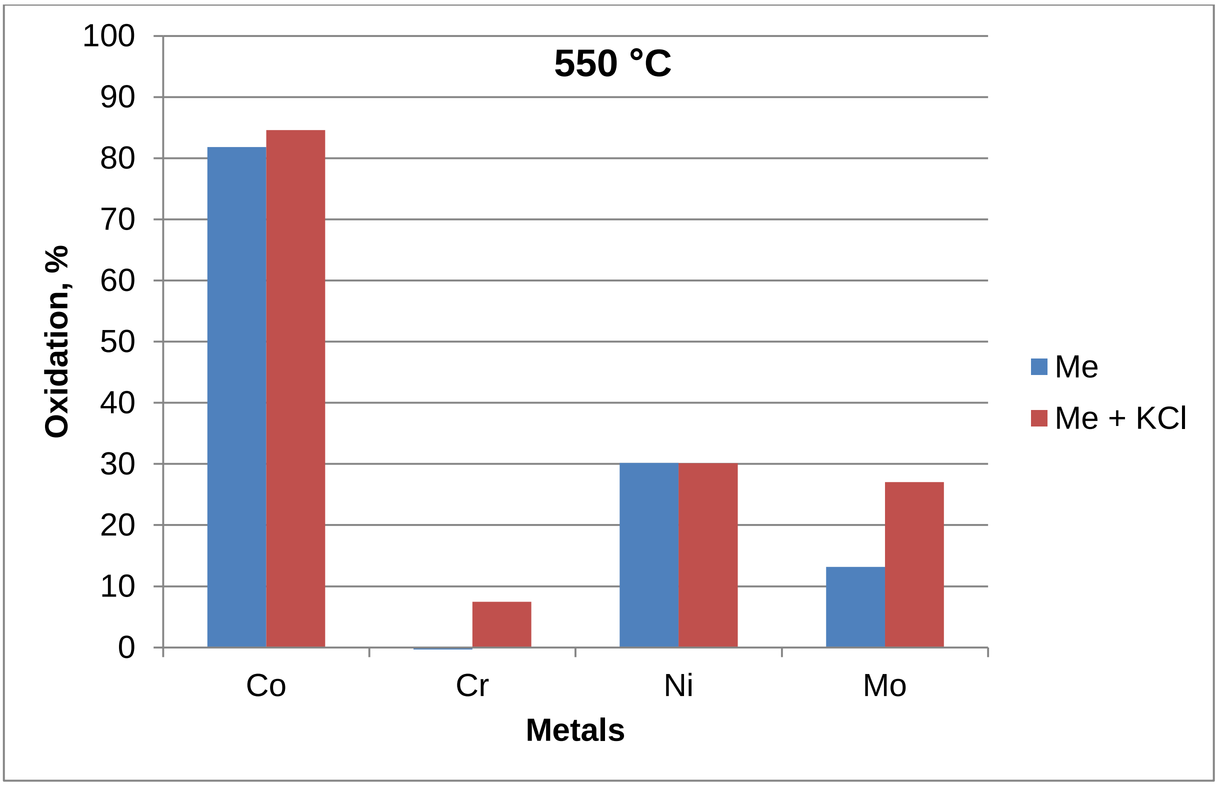

Figure 5.11. Relative oxidation of metals with and without potassium chloride at 550 °C.

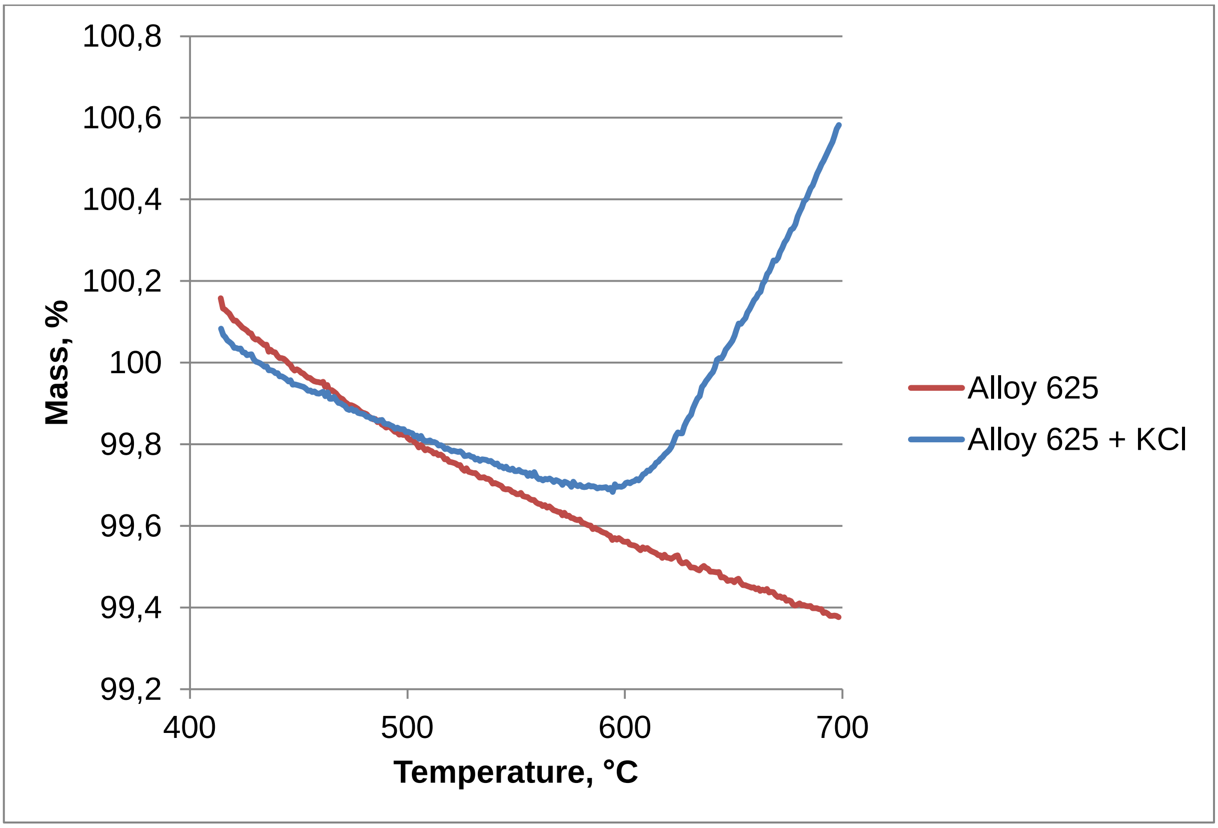

Figure 5.12. Thermogravimetry results for Alloy 625 with corrections.

Cobalt is totally oxidized already at about 470 °C in both cases (see Figure 5.5 and 5.6) – in single state and within salt mixture. The limit of oxidation is clearly seen – the curve becomes flat after 470 °C and show 81.83 and 84.59 % of oxidation at 550 °C for average data of runs (Figure 5.11). Generally, as the nickel samples cobalt experience the same level of oxidation with and without potassium chloride – no acceleration. Thus, in comparison to nickel cobalt has higher rate of corrosion (see Table 5.4) and for example at 550 °C it has 84.59 % against 30.15 % for the nickel, which is 2.8 times higher (Figure 5.11).

The worst result for chlorine induced oxidation is derived for molybdenum which undergoes high oxidation simultaneously with evaporation. Thus, at 550 °C it experiences 27.02 % of oxidation that is even smaller than in case of nickel, but already reaches complete oxidation at 570 °C (Figure 13). Following increase of temperature gives clearly detectible evaporation of the sample – decrease of the mass starts. Nevertheless, oxidation of single molybdenum shows good results in the range of 400-550 °C, and is in the level of 13.16 % at 550 °C, which is about twice lower than in case of single nickel. However, molybdenum achieves total oxidation already at 630 °C – curve reaches plateau and stays flat (Figure 11). Also, molybdenum has a good synergetic effect to hot corrosion resistance within Alloy 625.

Outstanding protective ability of Alloy 625 against oxidation and deposit corrosion is drawn by Figure 5.12. In case of inability to calculate relative oxidation rate for Alloy 625 due to complicated composition, the evaluation of its behavior can be made by comparing of gain of the samples mass related to formation of oxides. Thus, the level of mass gain in presence of potassium chloride even at 700 °C is 1.84 % comparing to 0.59 % in the single metal run (Figure 5.12). Additionally, the chlorine induced corrosion shows mass change of 0.61 % at 610 °C with following increase of oxidation rate – change of curve’s slope (Figure 21).

Summarizing, best results in hot corrosion resistance are achieved by Alloy 625 and nickel. The level of oxidations that the listed samples form protective oxide scales in the whole range of studied temperatures (400-700 °C). Chromium shows inertness to presence of potassium chloride, but could be applicable as superheater material up to 550-600 °C. In the same time cobalt also shows the inertness to deposit corrosion, but it forms porous non protective layer already at 450 °C. Finally, molybdenum could find application up to 530-540 °C because the evaporation of molybdenum chloride starts in this temperature range causing no protection to corrosion.

6. CONCLUSIONS

The utilization of biomass in fluidized bed provides specific boiler environment. Thus, temperature range near surfaces of heat exchangers is about 550-600 °C. Moreover, biomass contains higher level of halogens, alkali and heavy metals compare to fossil fuel. That is why its utilization provides highly corrosive conditions within boiler environment. The most crucial compound providing accelerated corrosion is potassium chloride. Thus, deposits containing potassium chloride settle on heat exchange surfaces where chlorine acts as a catalyst for oxidation of metal surfaces.

The overview of corrosion mechanism draws that protection is obtained due to formation of tight and dense oxide layer on the metal surface exposed to corrosive atmosphere. The performed study of currently used ferrous materials shows that they form weak protective oxide scale. However, materials containing non ferrous alloying elements demonstrate increased corrosion resistance by formation of corresponding metal oxides. Therefore, chromium, cobalt, nickel, molybdenum, Alloy 625 were chosen as perspective materials for utilization in tubes and coatings of boiler pressure parts.

The main results obtained from performed experimental study of non ferrous materials shown that. The best resistance to chlorine induced corrosion is possessed by Alloy 625. Than resistance properties are reduced in the range of single metals: nickel, chromium, molybdenum and cobalt. It should be noted that single metals with poor resistance properties (e.g. molybdenum) could show excellent synergetic resistance within the alloys due to formation of complicated oxide layer structure.

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APPENDIX 1

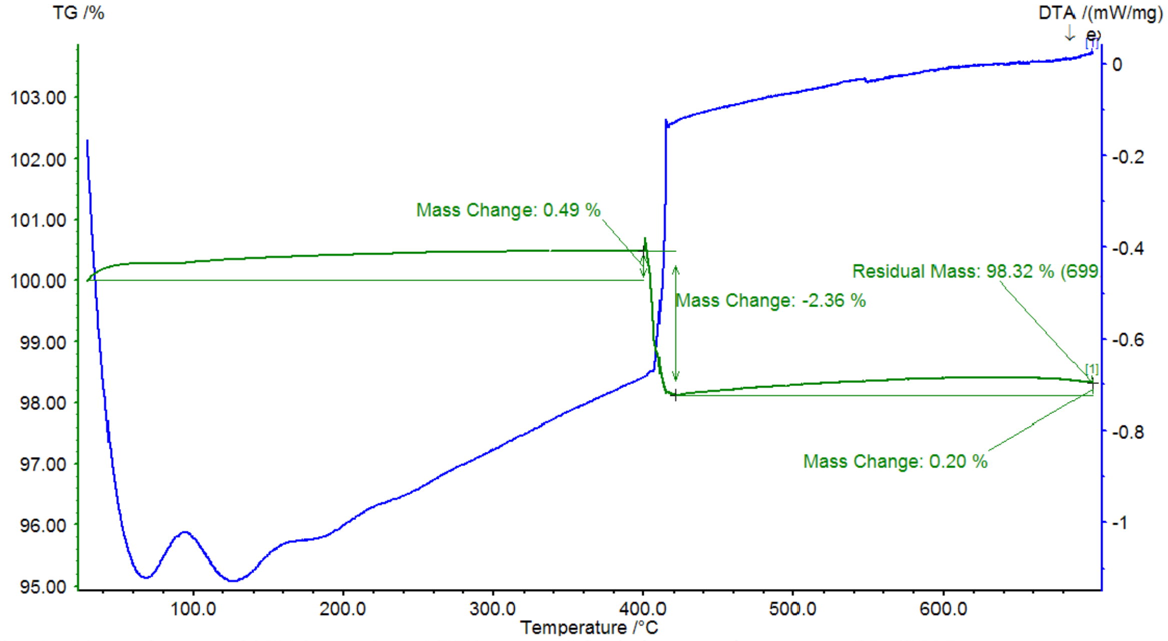

Fig. 1a Mass change of KCl (green) and DTA-curve (blue), temperature range 25-700°C.

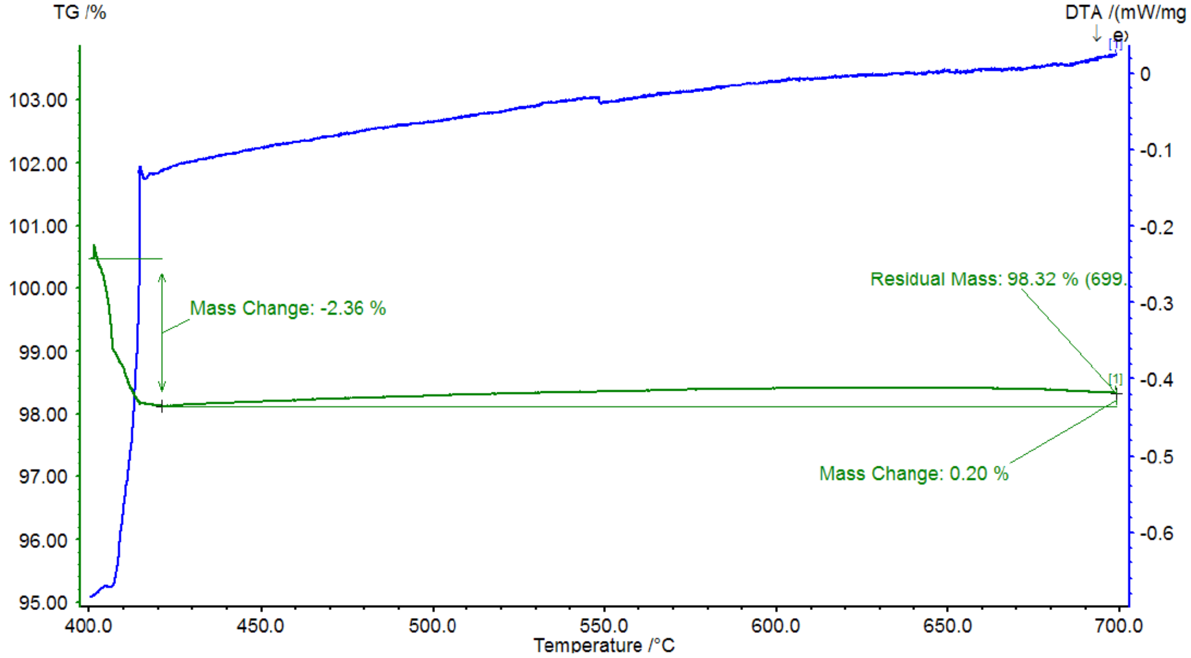

Fig. 1b Mass change of KCl (green) and DTA-curve (blue), temperature range 400-700°C.

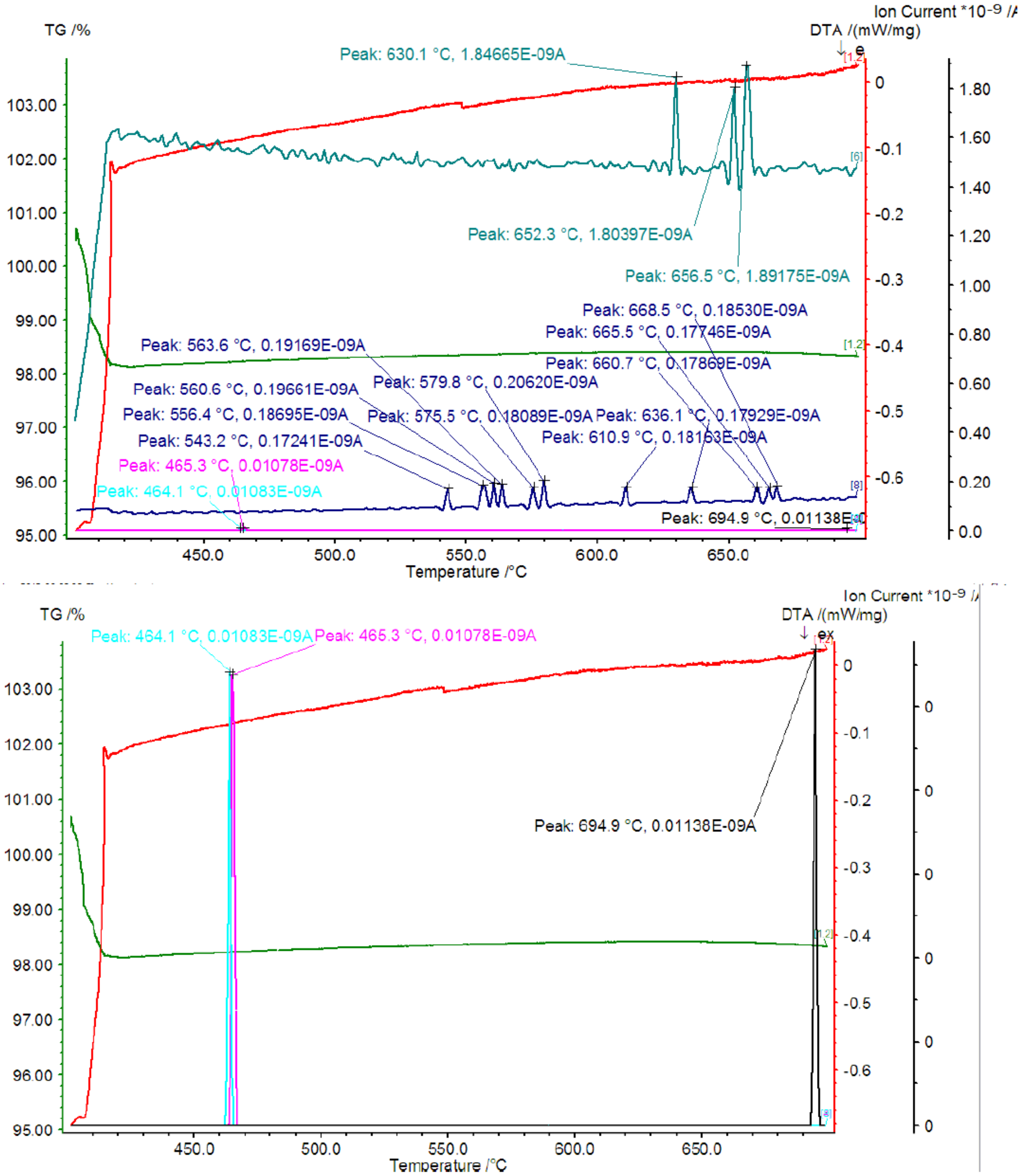

Fig. 2 Mass change of KCl (green) and DTA-curve (red) and gases formed during burning C (pink, 12 amu), O (grey, 16 amu), H_2O (blue, 18 amu), Al (turquoise 25 amu).

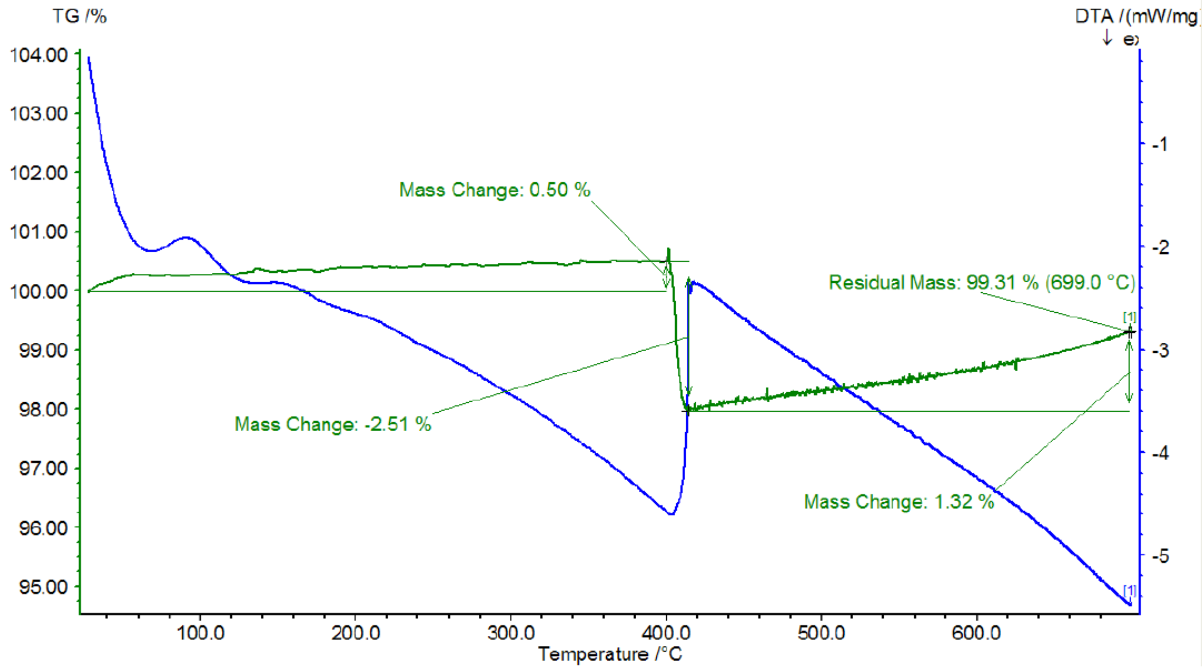

Fig. 3a Mass change of Cr (green) and DTA-curve (blue), temperature range 25-700°C.

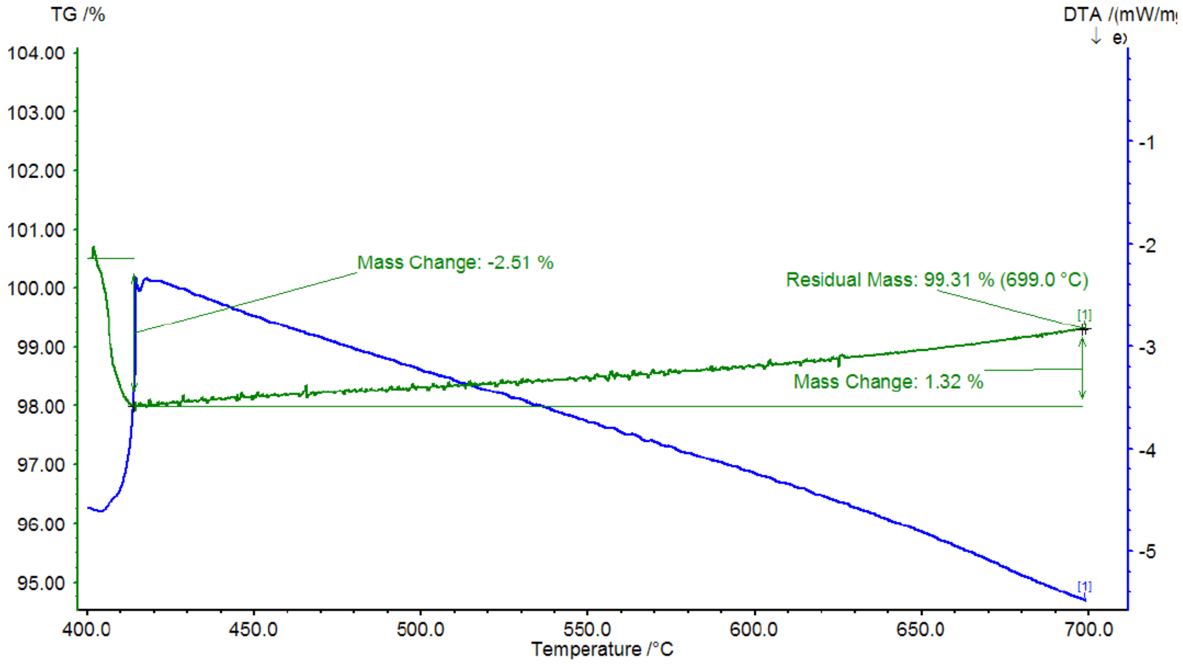

Fig. 3b Mass change of Cr (green) and DTA-curve (blue), temperature range 400-700°C.

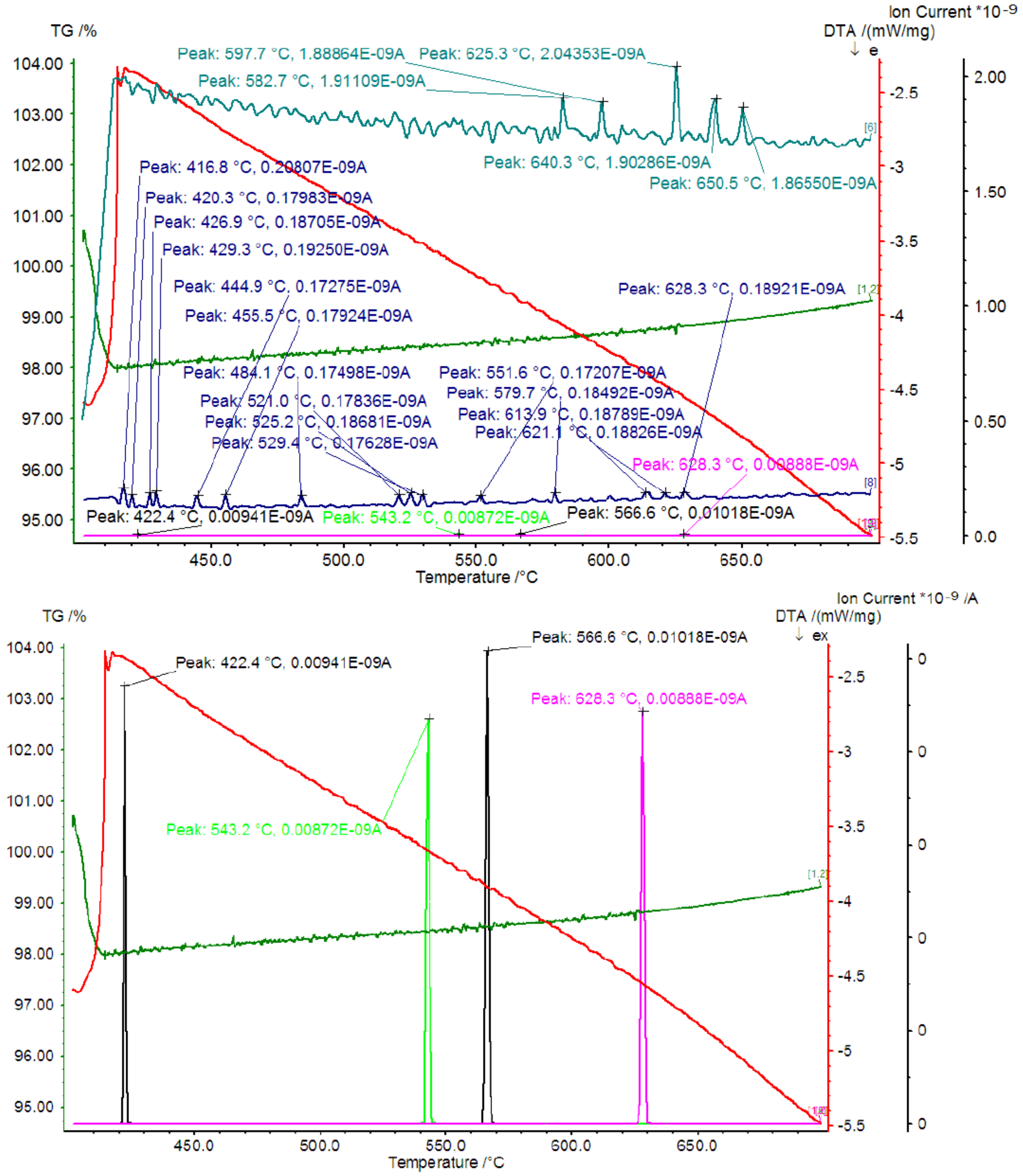

Fig. 4 Mass change of Cr (green) and DTA-curve (red) and gases formed during burning (black, 5 amu), C (neon green, 12 amu), O (grey, 16 amu), H_2O (dark blue, 18 amu), Al (pink, 25 amu).

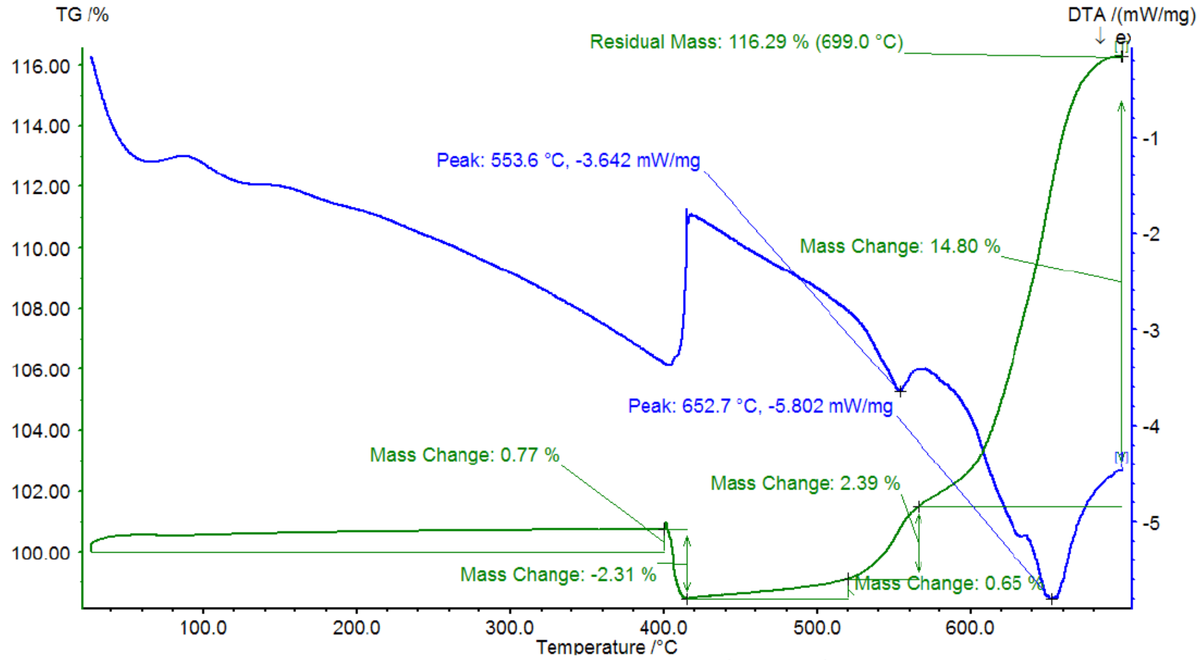

Fig. 5a Mass change of Cr+KCl (green) and DTA-curve (blue), temperature range 25-700°C.

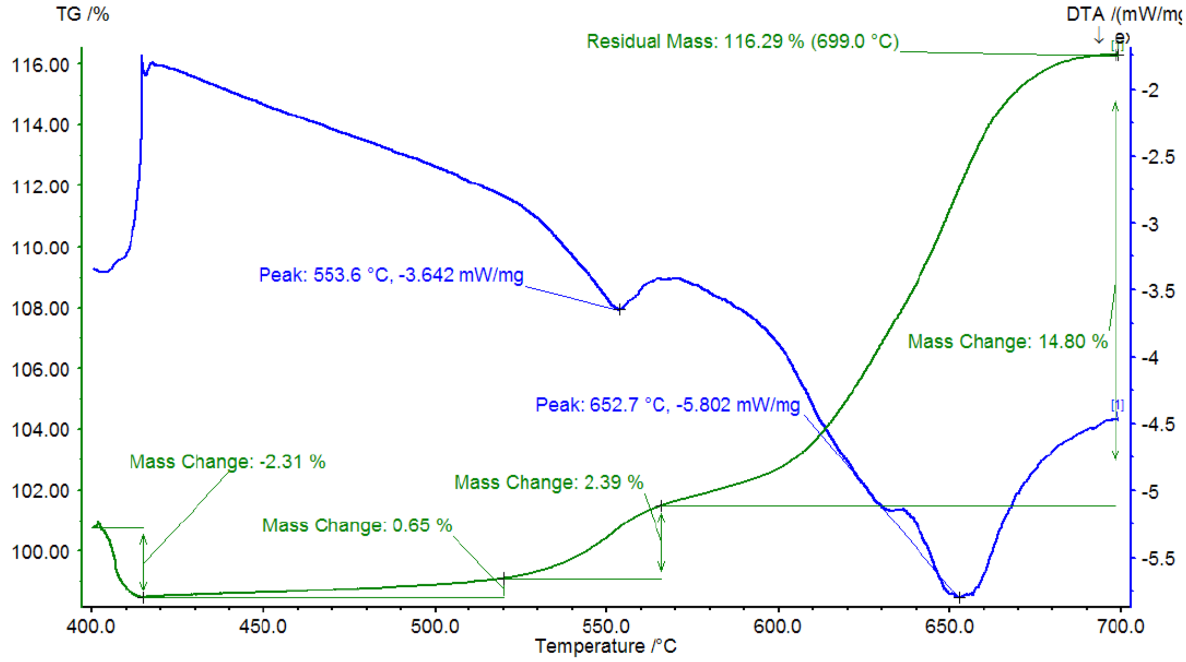

Fig. 5b Mass change of Cr+KCl (green) and DTA-curve (blue), temperature range 400-700°C.

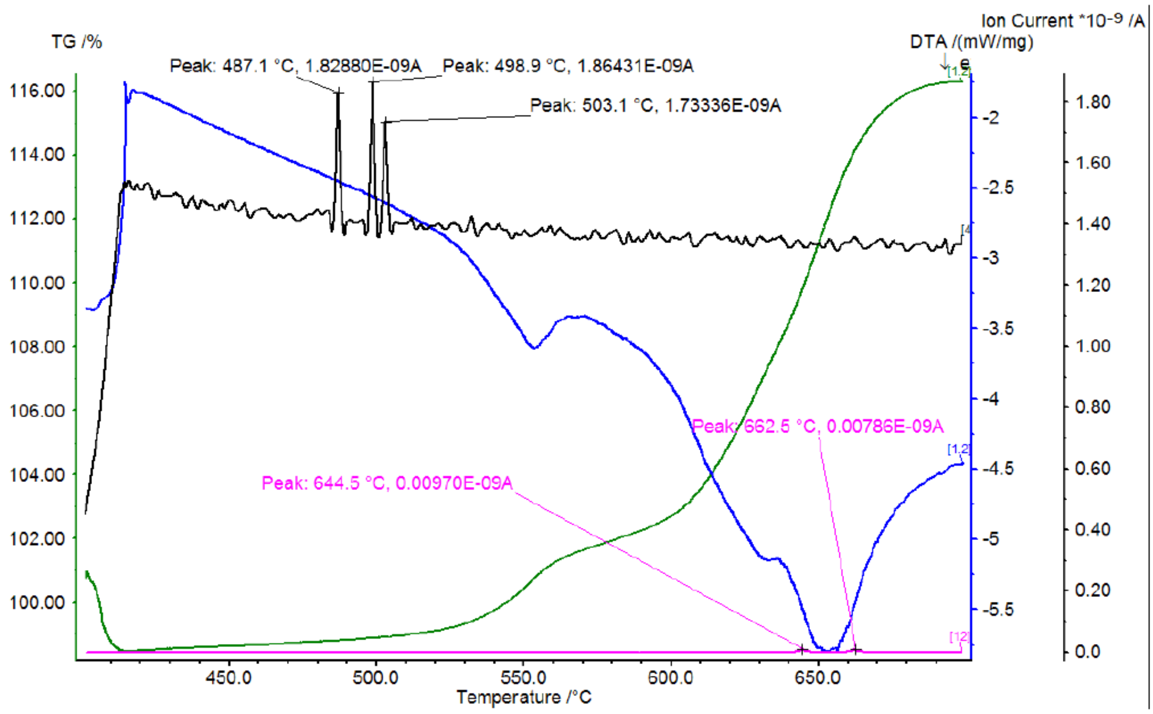

Fig 6 Mass change of Cr+KCl (green) and DTA-curve (blue) and gases formed during burning O (black, 16 amu), CO_2 (pink, 44 amu).

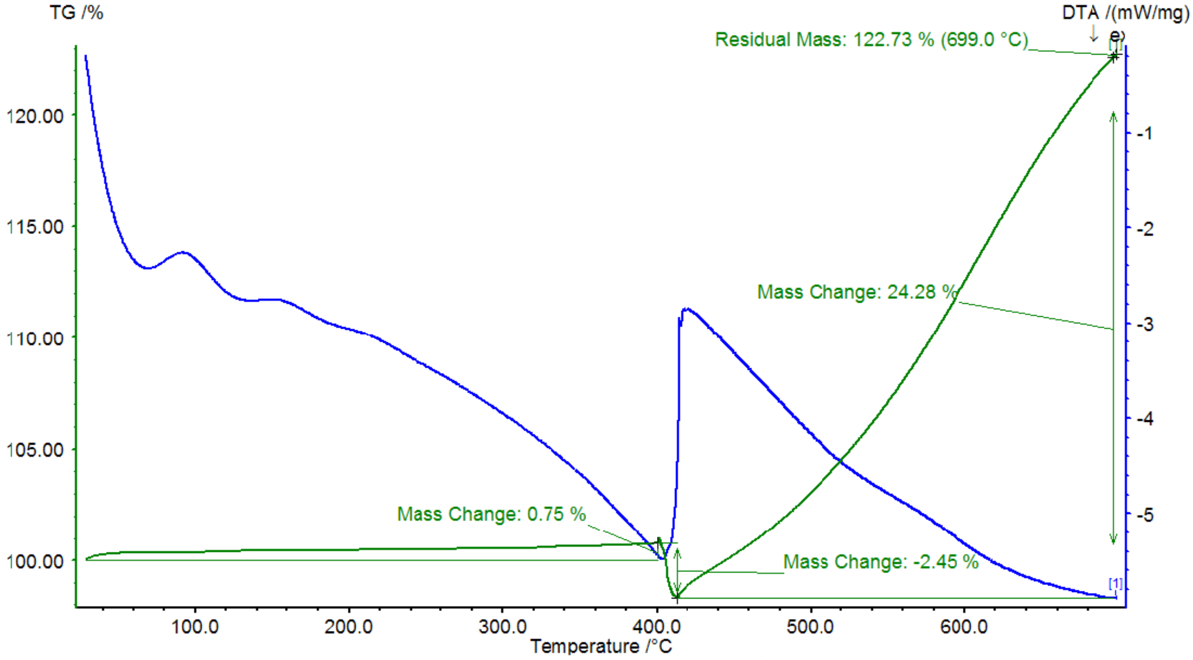

Fig. 7a Mass change of Ni (green) and DTA-curve (blue), temperature range 25-700°C.

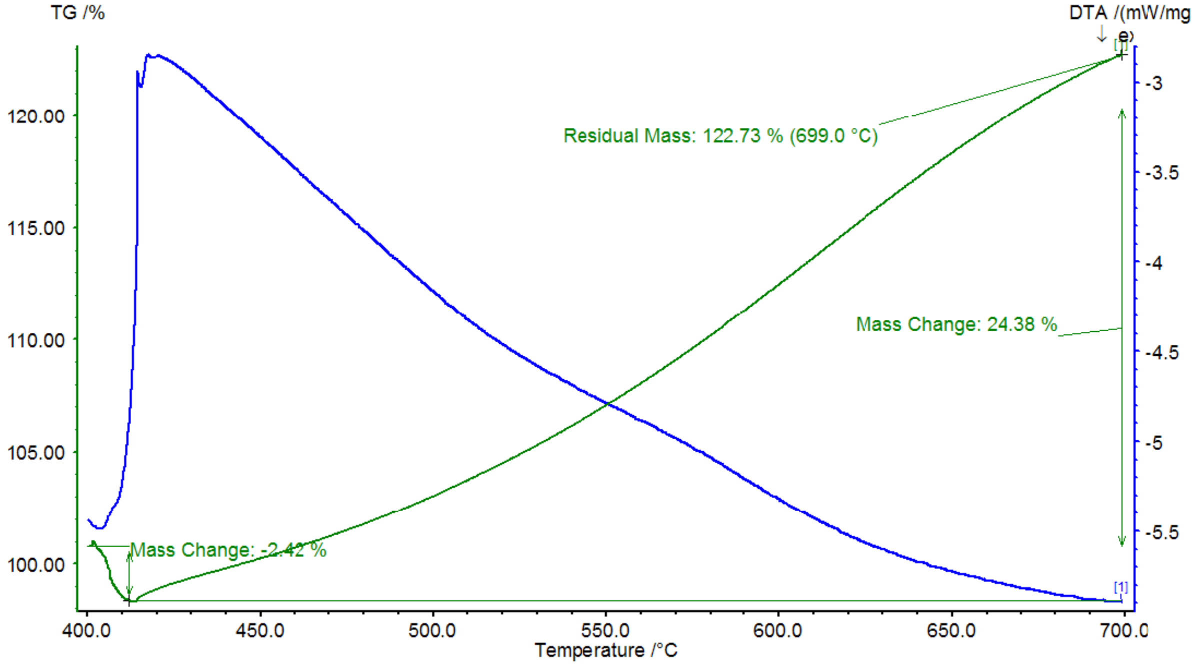

Fig. 7b Mass change of Ni (green) and DTA-curve (blue), temperature range 400-700°C.

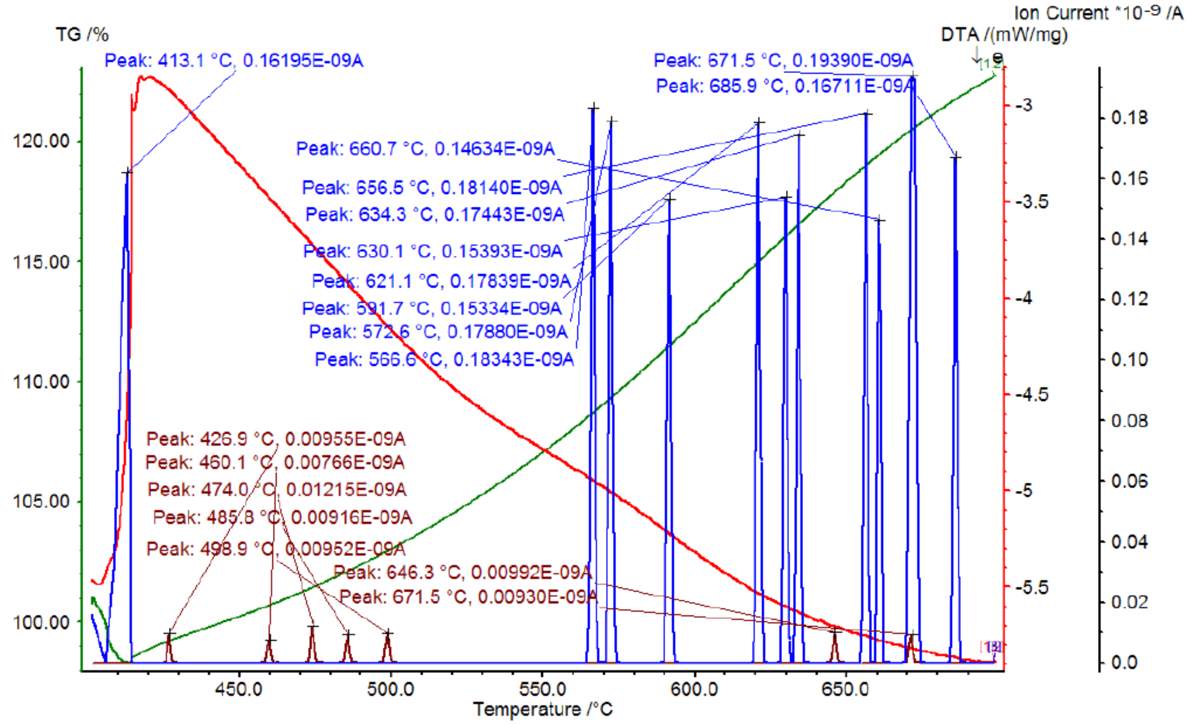

Fig 8 Mass change of Ni (green) and DTA-curve (red) and gases formed during burning He (brown, 5 amu), OH, O (blue, 17 amu).

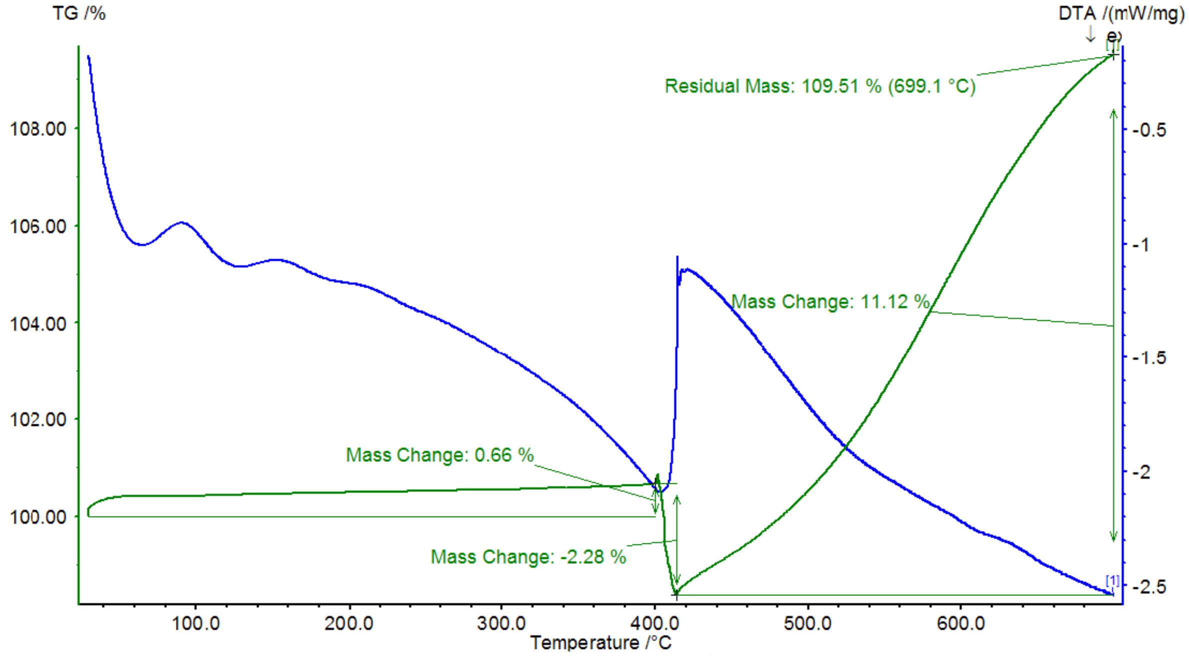

Fig. 9a Mass change of Ni+KCl (green) and DTA-curve (blue), temperature range 25-700°C.

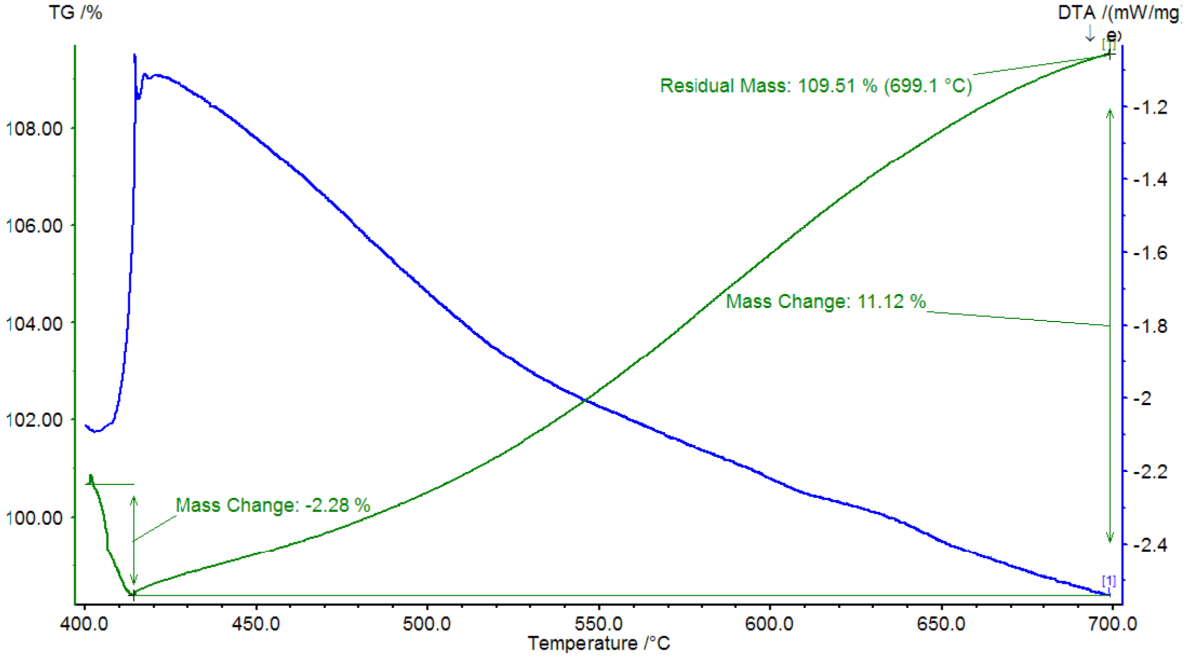

Fig. 9b Mass change of Ni+KCl (green) and DTA-curve (blue), temperature range 400-700°C.

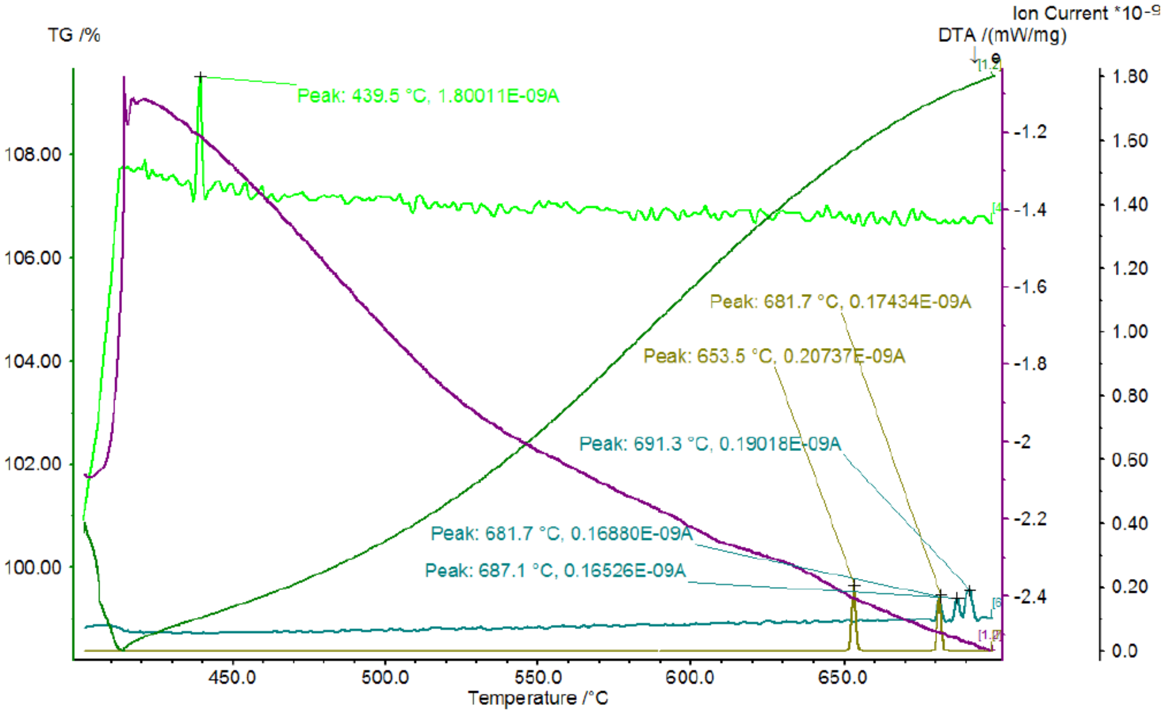

Fig 10 Mass change of Ni+KCl (green) and DTA-curve (purple) and gases formed during burning O (neon green, 16 amu), H_2O ('grey', 18 amu), Al (moss green, 26 amu).

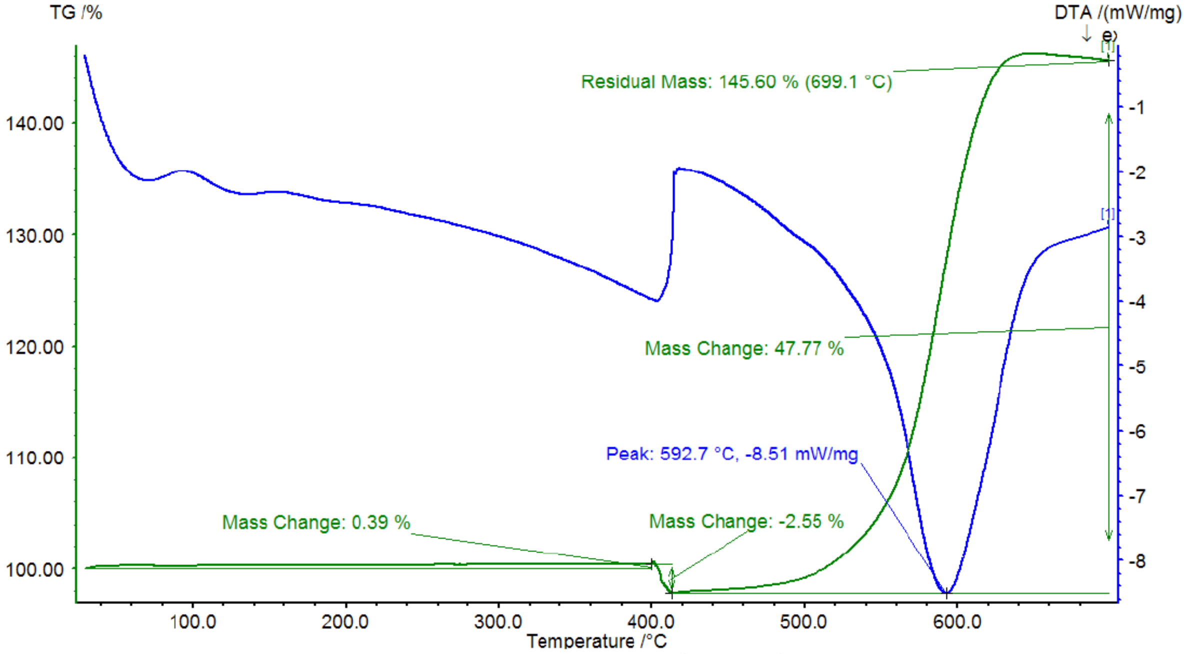

Fig. 11a Mass change of Mo (green) and DTA-curve (blue), temperature range 25-700°C.

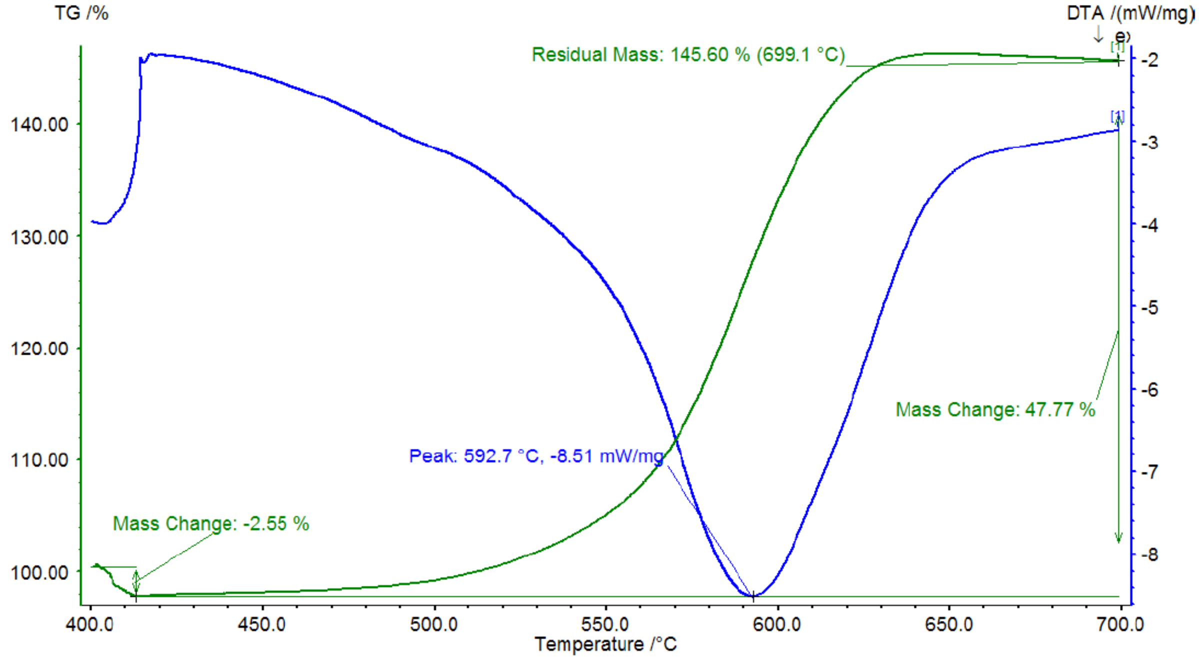

Fig. 11b Mass change of Mo (green) and DTA-curve (blue), temperature range 400-700°C.

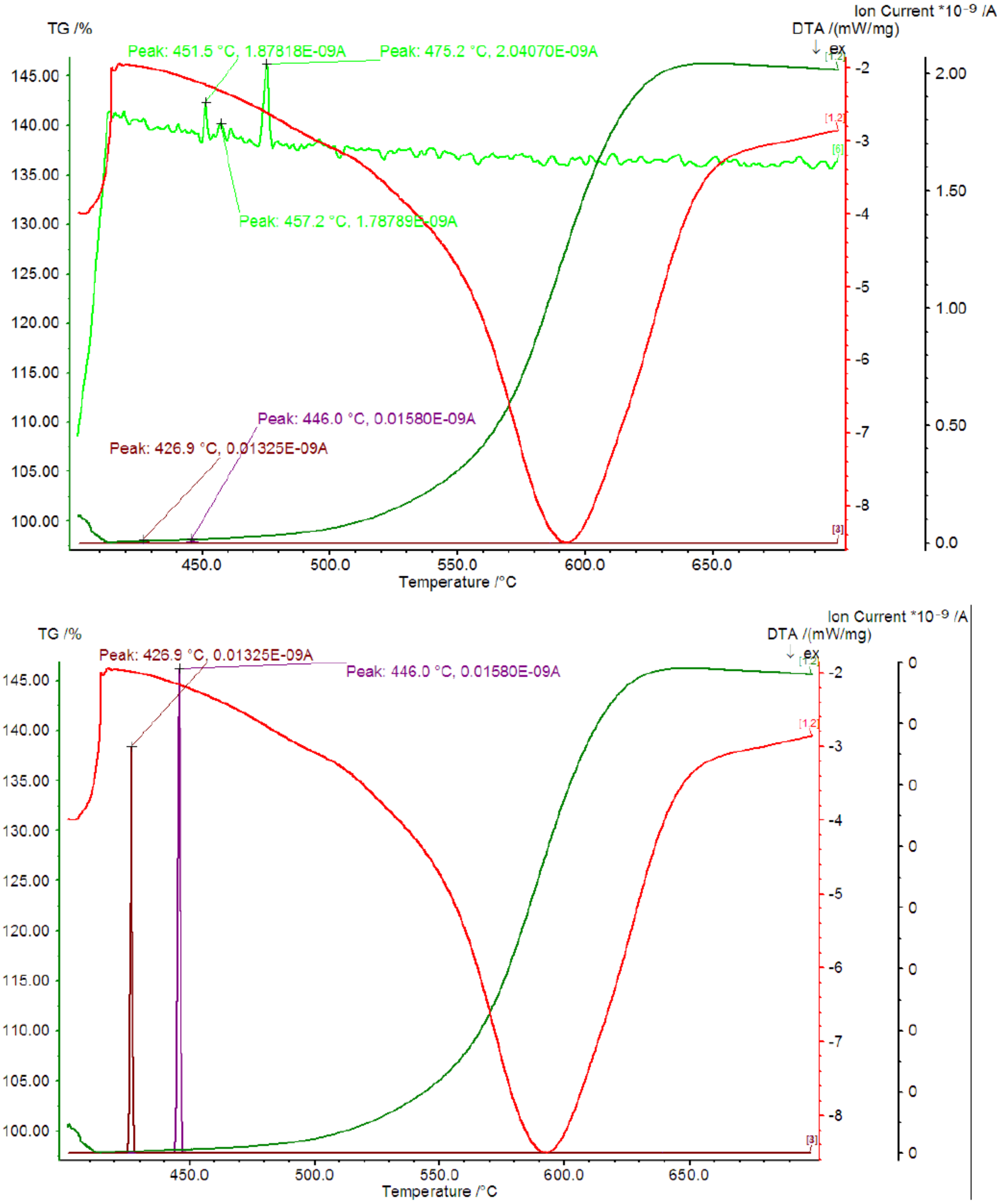

Fig 12 Mass change of Mo (green) and DTA-curve (red) and gases formed during burning He (purple, 5 amu), C (brown, 12 amu), O (neon green, 16 amu).

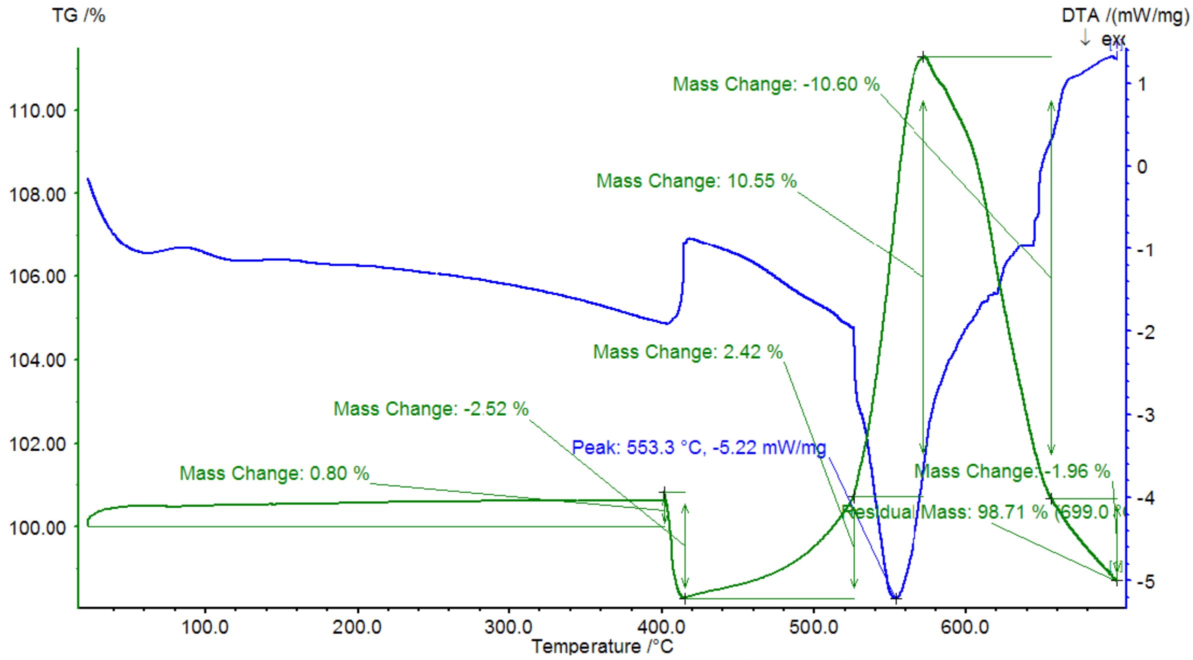

Fig. 13a Mass change of Mo+KCl (green) and DTA-curve (blue), temperature range 25-700°C.

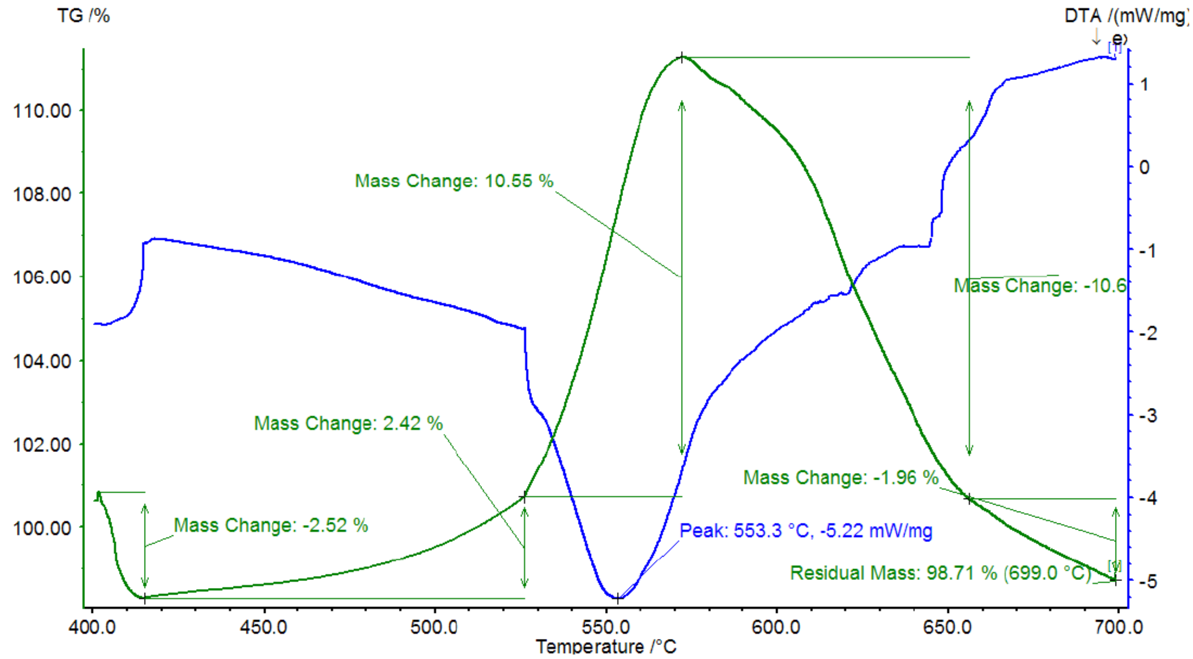

Fig. 13b Mass change of Mo+KCl (green) and DTA-curve (blue), temperature range 400-700°C.

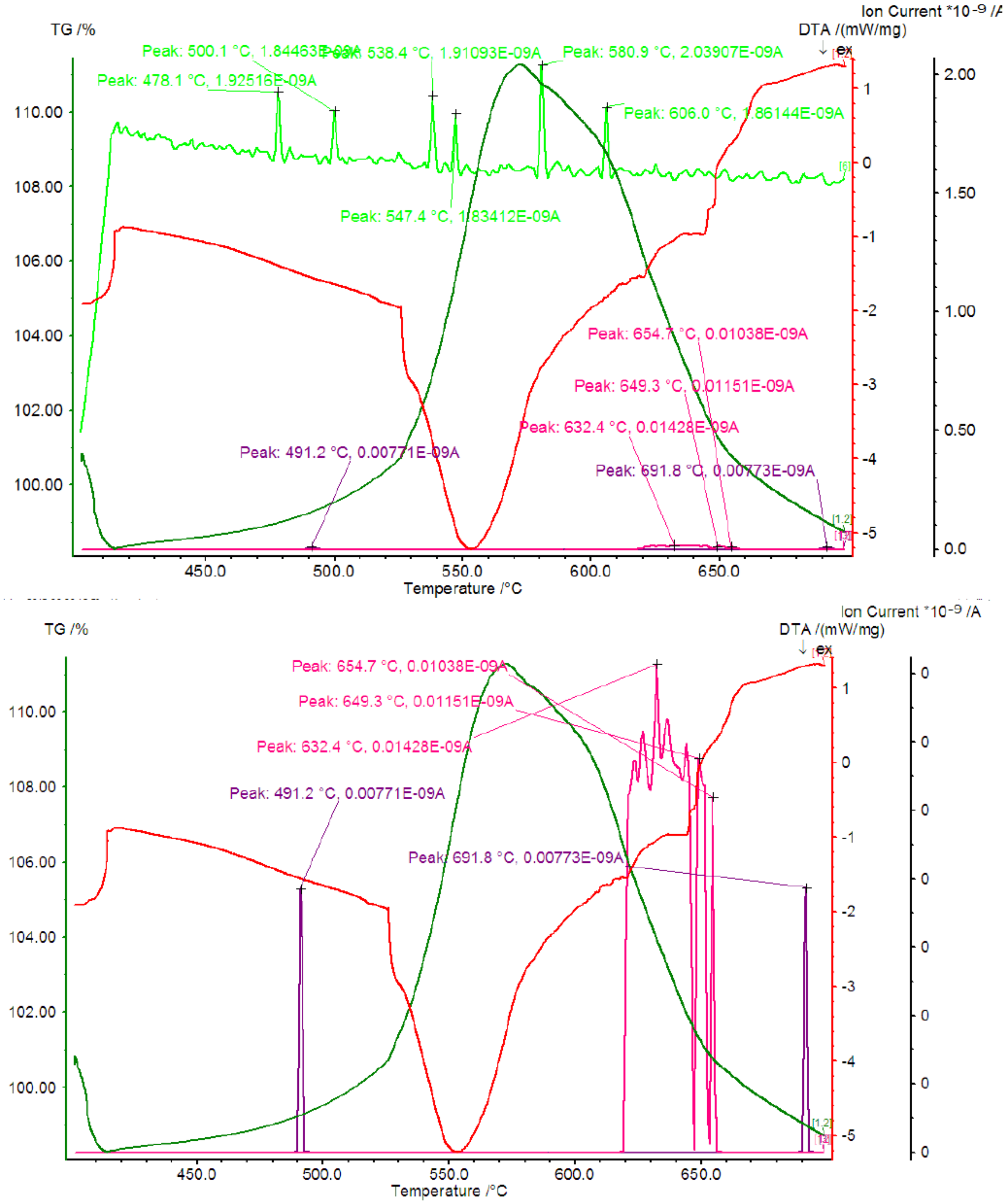

Fig 14 Mass change of Mo+KCl (green) and DTA-curve (red) and gases formed during burning He (purple, 5 amu), O (neon green, 16 amu), Cl (pink, 36 amu).

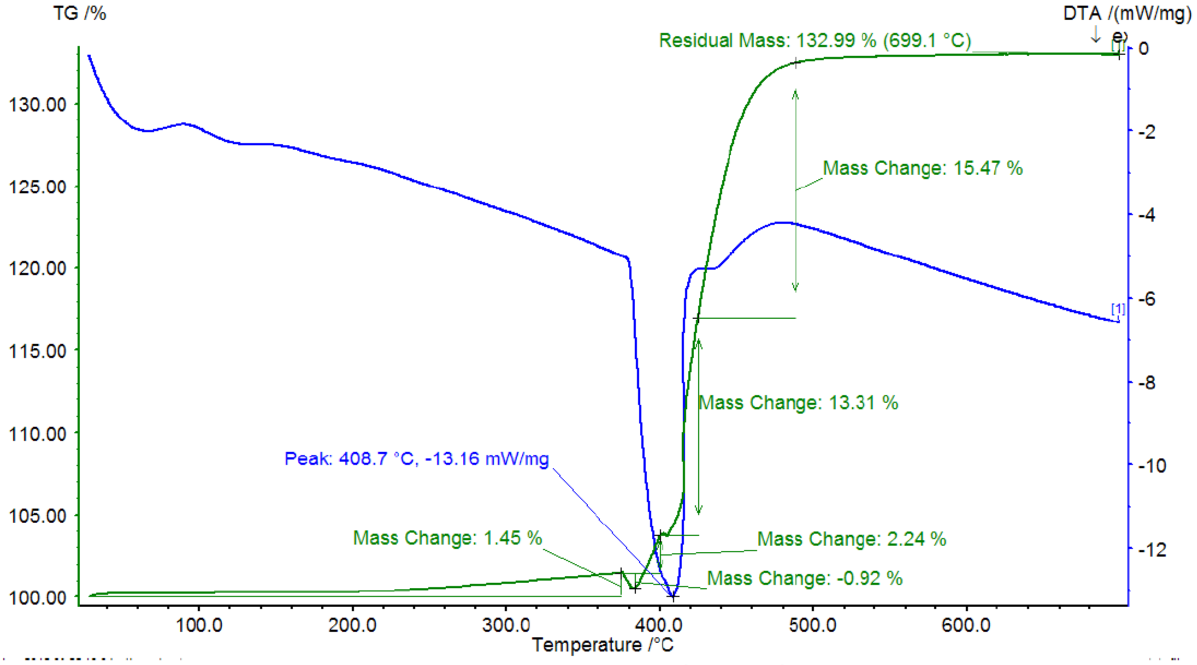

Fig.15a Mass change of Co (green) and DTA-curve (blue), temperature range 25-700°C.

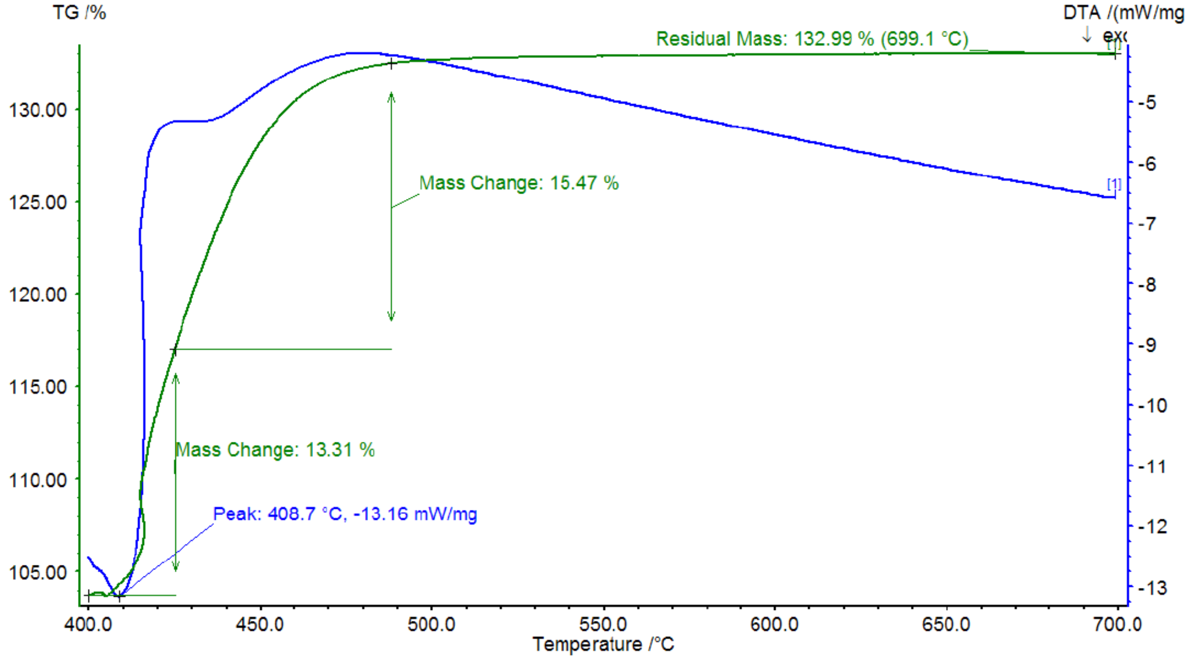

Fig.15b Mass change of Co (green) and DTA-curve (blue), temperature range 400-700°C.

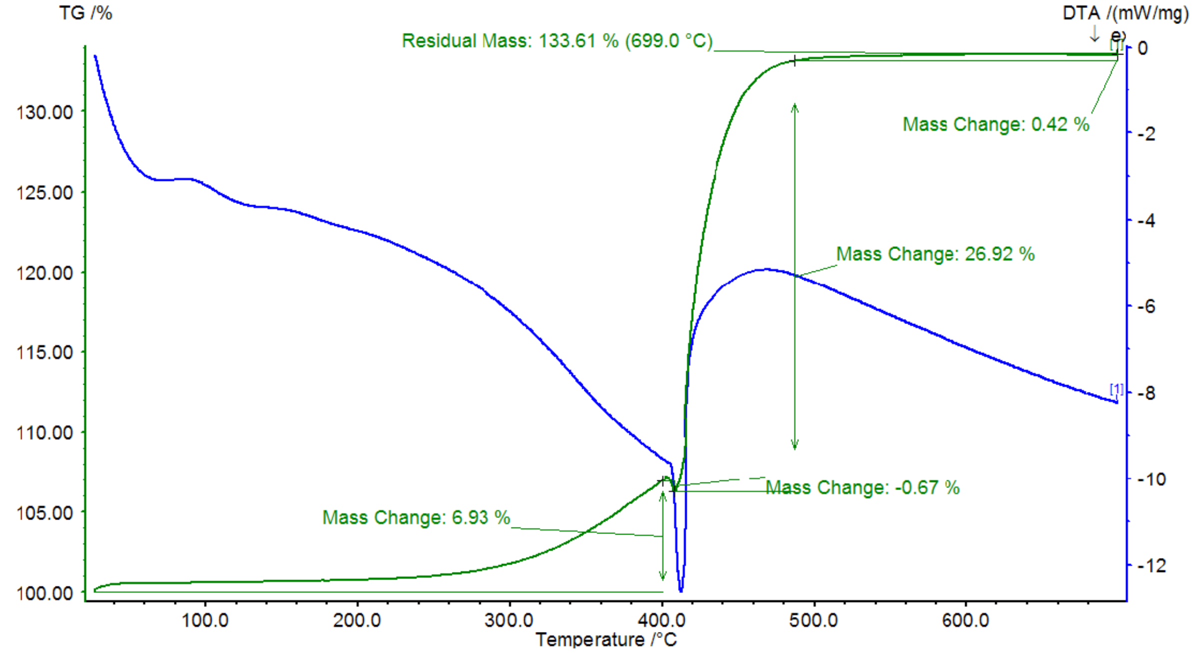

Fig.15c Mass change of Co (green) and DTA-curve (blue), temperature range 25-700°C.

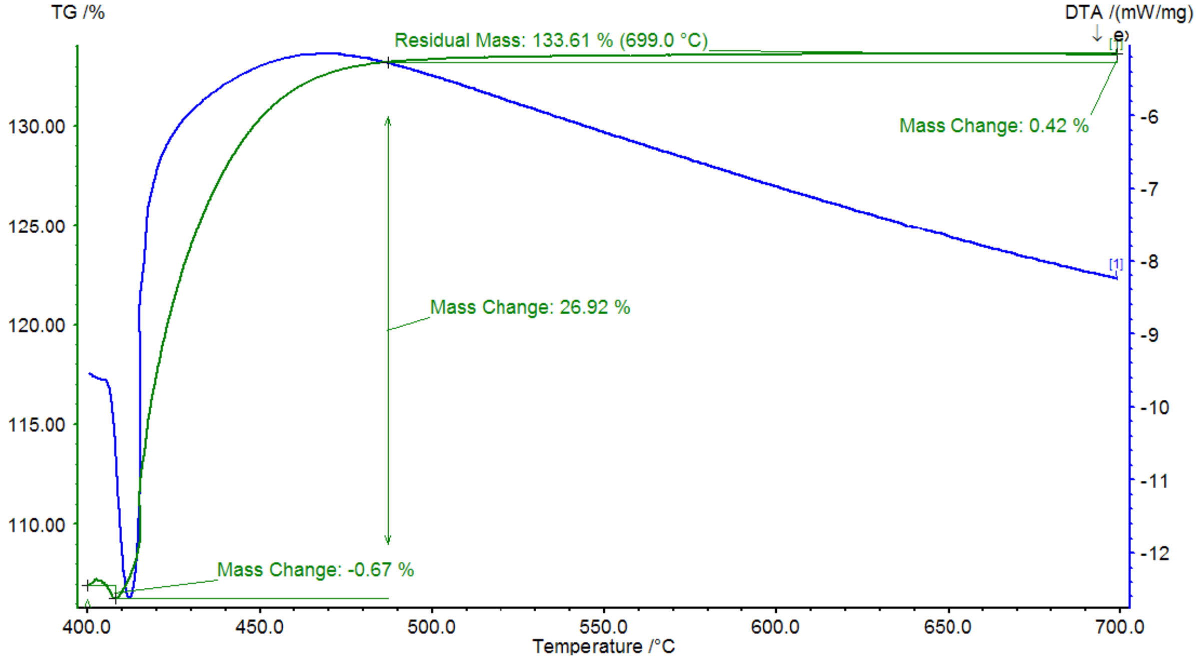

Fig.15d Mass change of Co (green) and DTA-curve (blue), temperature range 400-700°C.

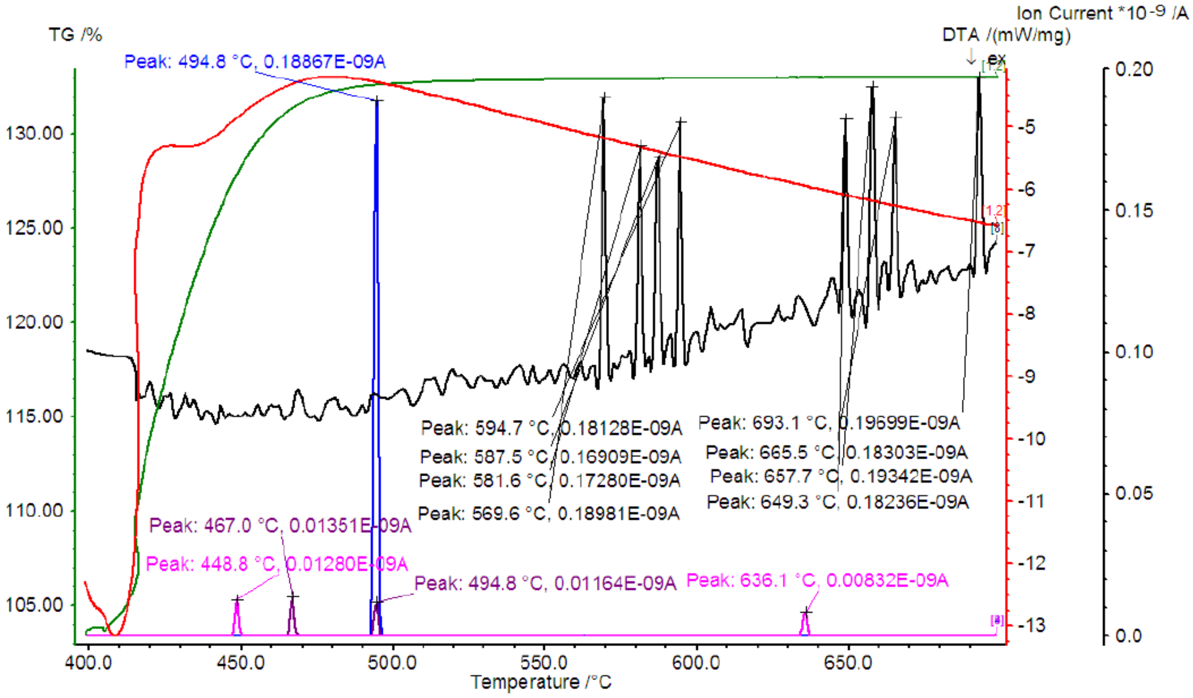

Fig. 16a Mass change of Co (green) and DTA-curve (red) and gases formed during burning He (purple, 5 amu), CH (blue, 13 amu), H_2O (black, 18 amu), Al (pink, 25 amu).

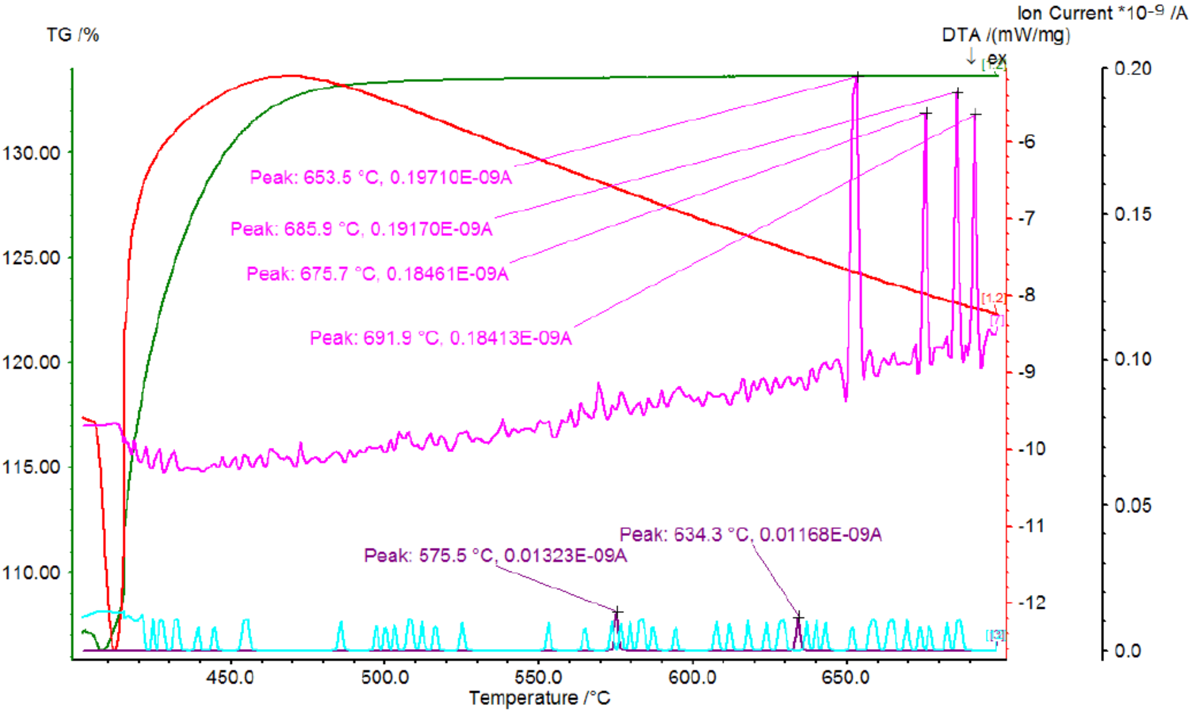

Fig 16b Mass change of Co (green) and DTA-curve (red) and gases formed during burning He (purple, 5 amu), H_2O (pink, 18 amu), CO_2 (turquoise 44 amu).

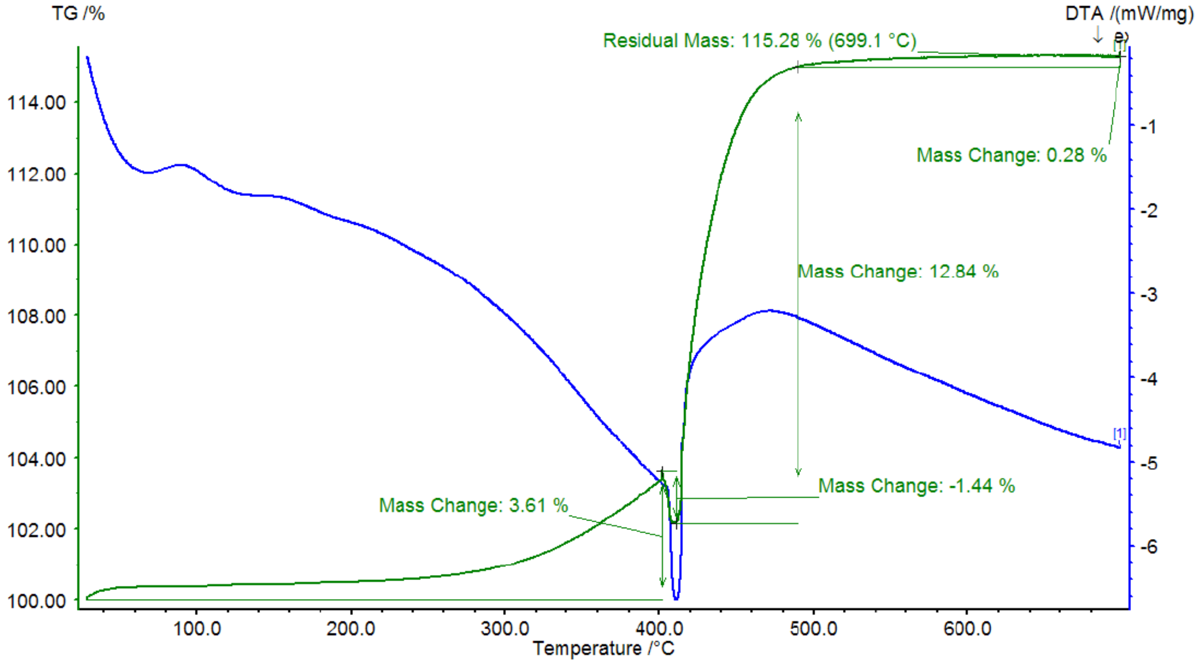

Fig. 17a Mass change of Co+KCl (green) and DTA-curve (blue), temperature range 25-700°C.

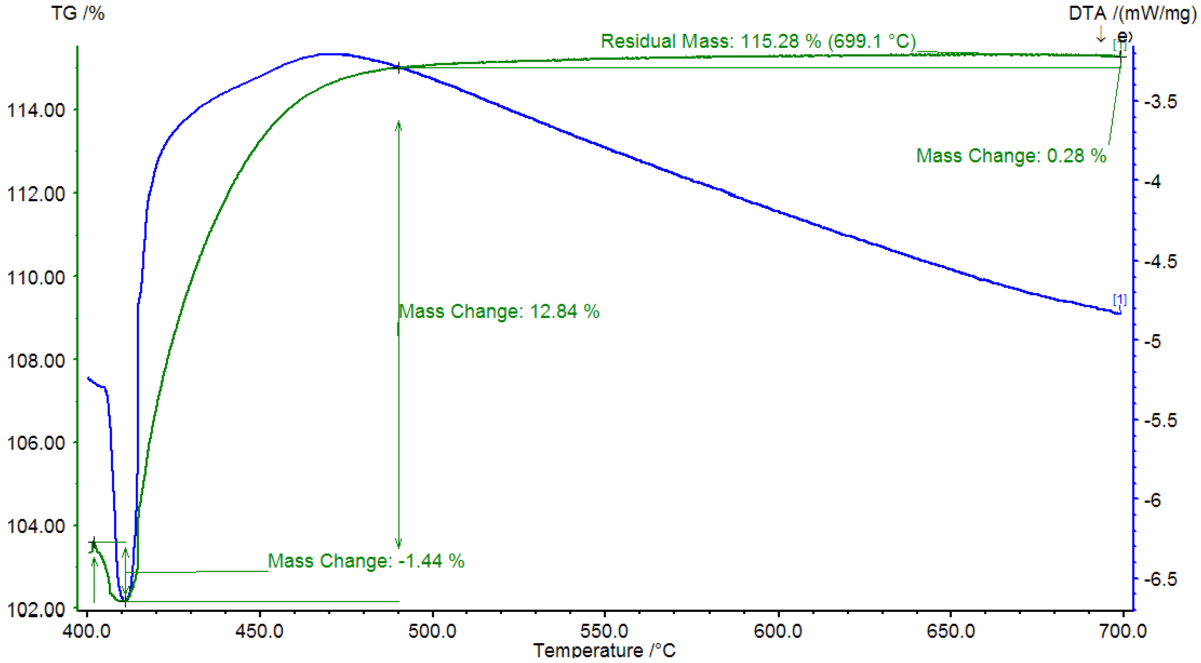

Fig. 17b Mass change of Co+KCl (green) and DTA-curve (blue), temperature range 400-700°C.

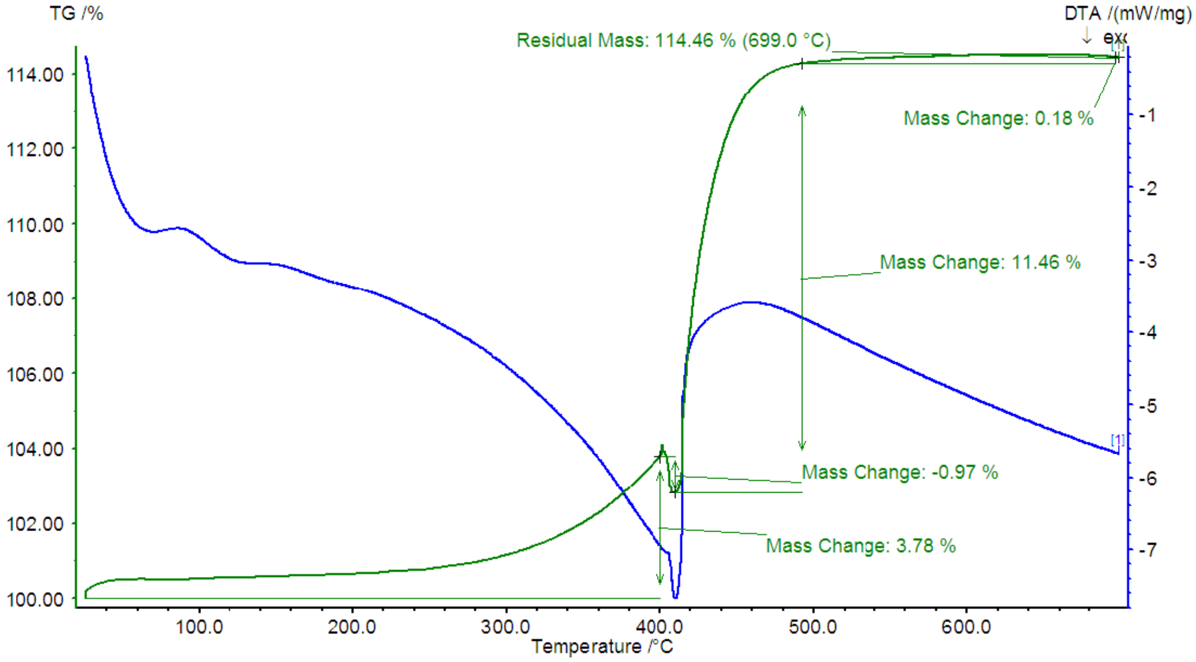

Fig. 17c Mass change of Co+KCl (green) and DTA-curve (blue), temperature range 25-700°C.

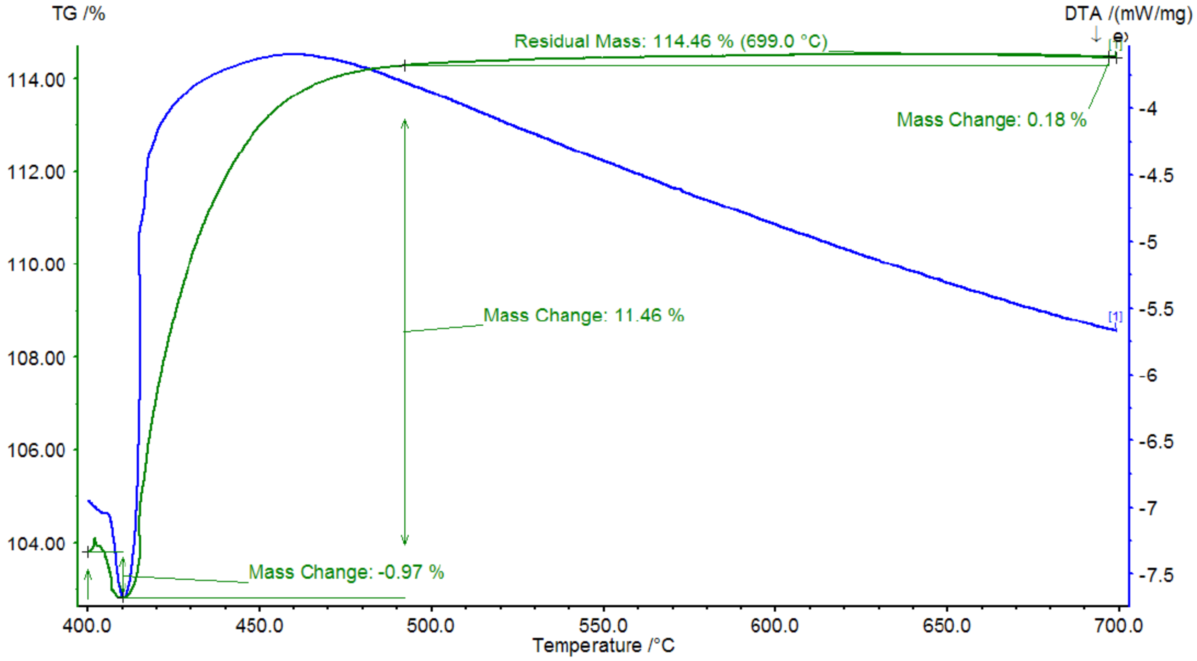

Fig. 17d Mass change of Co+KCl (green) and DTA-curve (blue), temperature range 400-700°C.

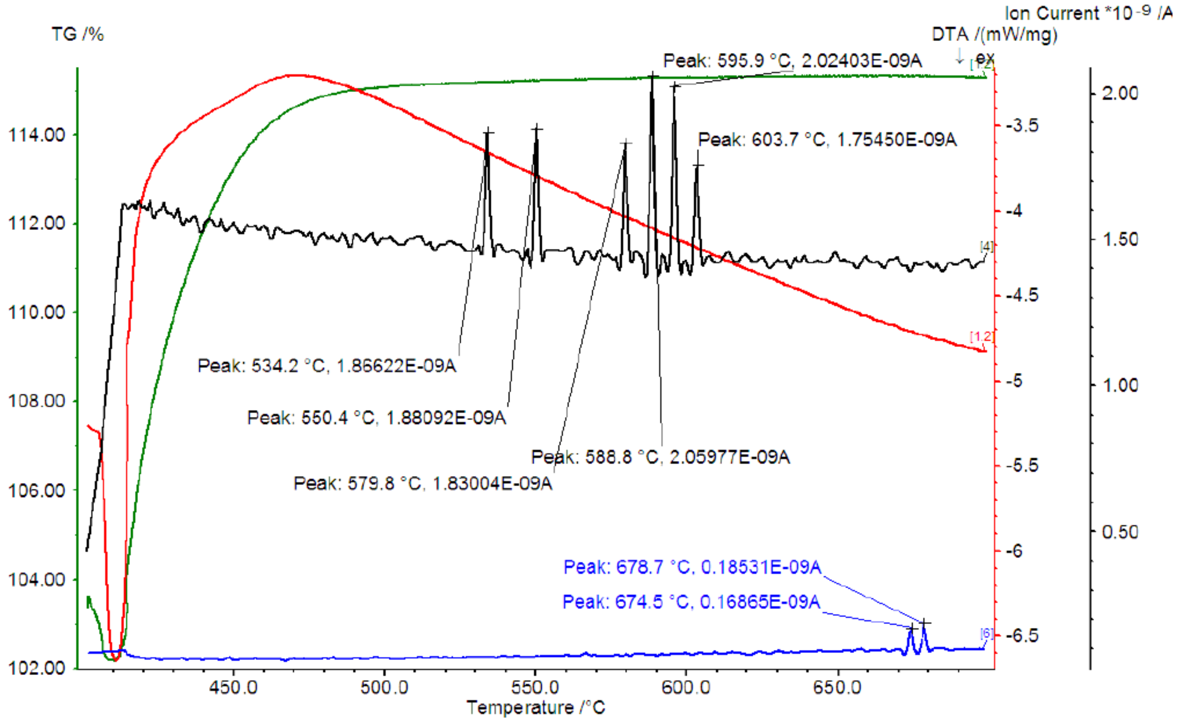

Fig. 18a Mass change of Co+KCl (green) and DTA-curve (red) and gases formed during burning O (black, 16 amu), H_2O (blue, 18 amu).

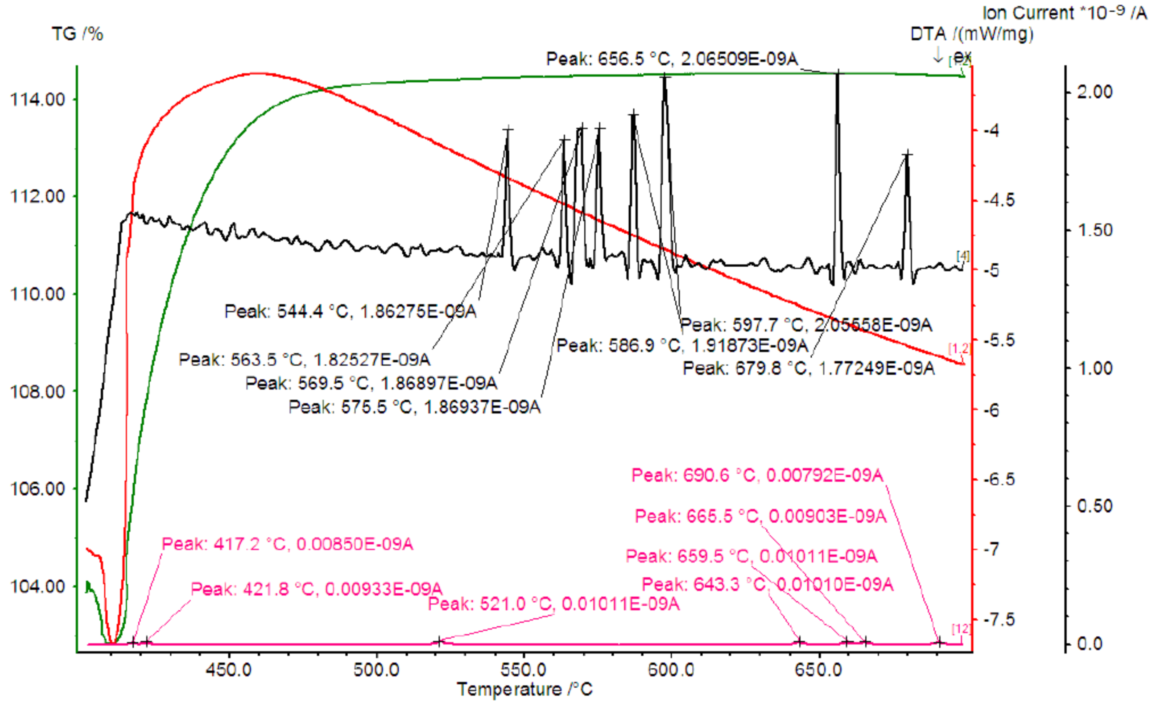

Fig. 18b Mass change of Co+KCl (green) and DTA-curve (red) and gases formed during burning O (black, 16 amu), CO_2 (fuchsia, 44 amu).

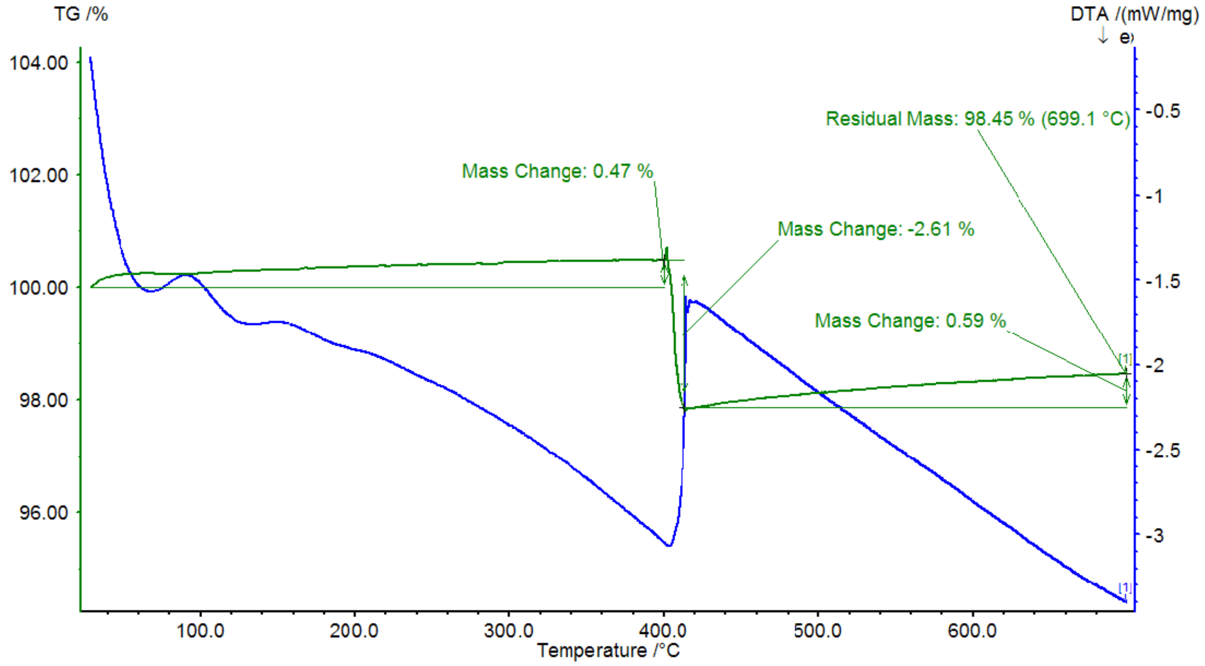

Fig. 19a Mass change of Alloy 625 (green) and DTA-curve (blue), temperature range 25-700°C.

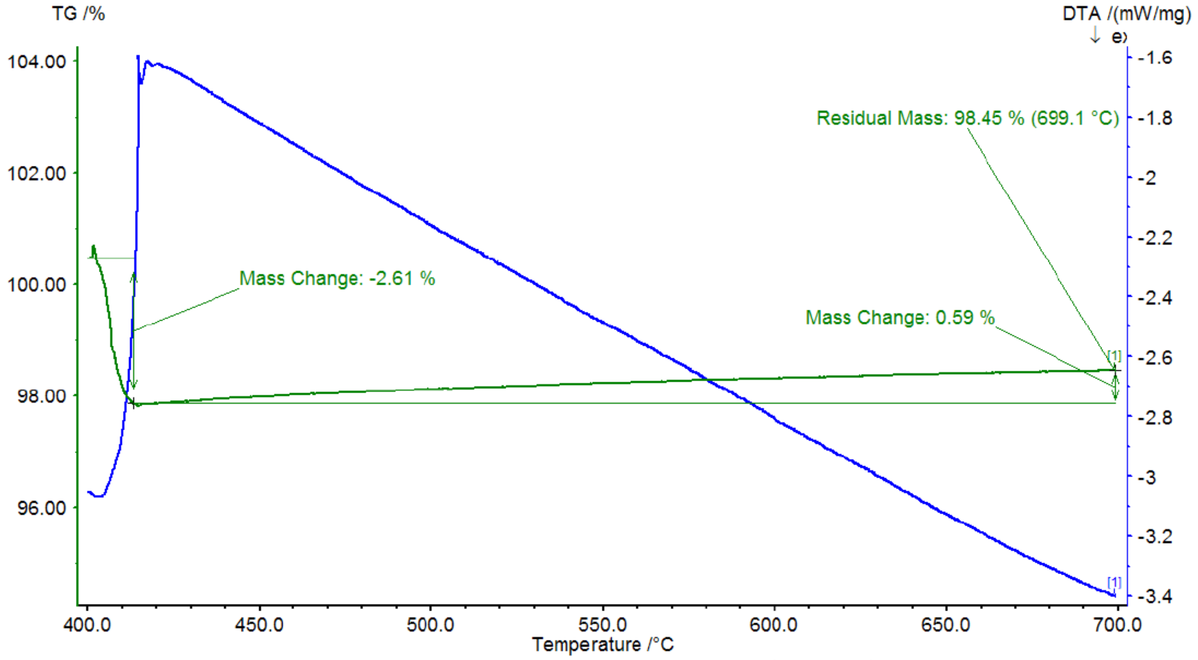

Fig. 19b Mass change of Alloy 625 (green) and DTA-curve (blue), temperature range 400-700°C.

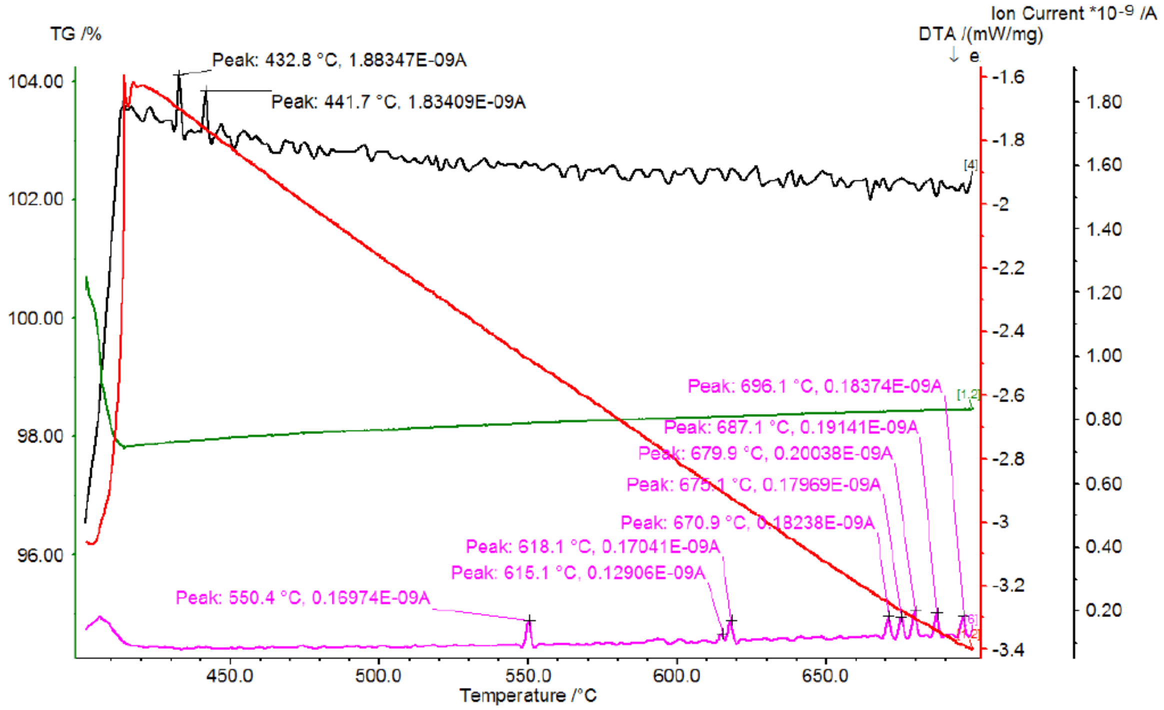

Fig 20 Mass change of Alloy 625 (green) and DTA-curve (red) and gases formed during burning O (black, 16 amu), H_2O (pink, 18 amu).

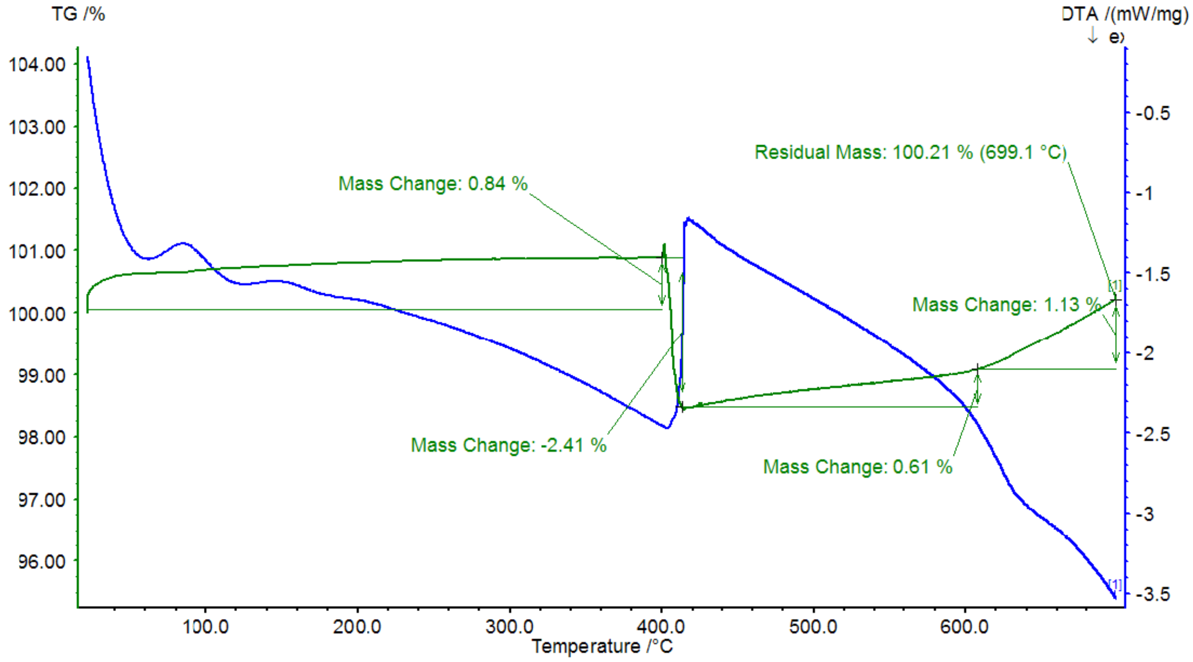

Fig. 21a Mass change of Alloy 625+KCl (green) and DTA-curve (blue), temperature range 25-700°C.

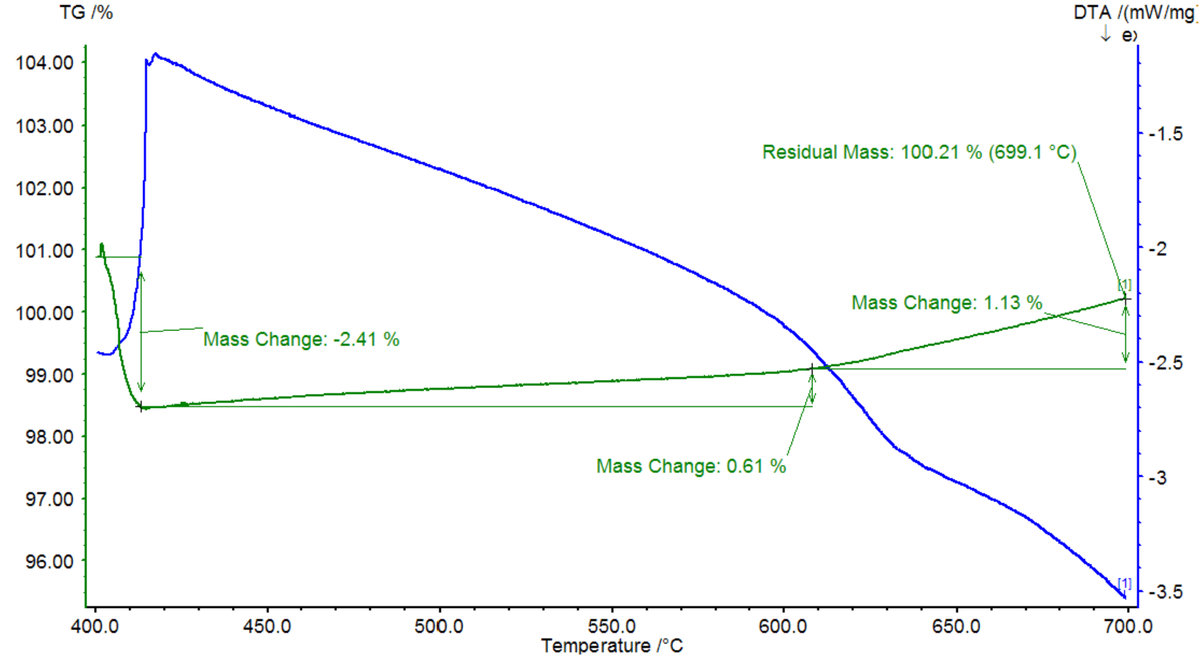

Fig. 21b Mass change of Alloy 625+KCl (green) and DTA-curve (blue), temperature range 400-700°C.

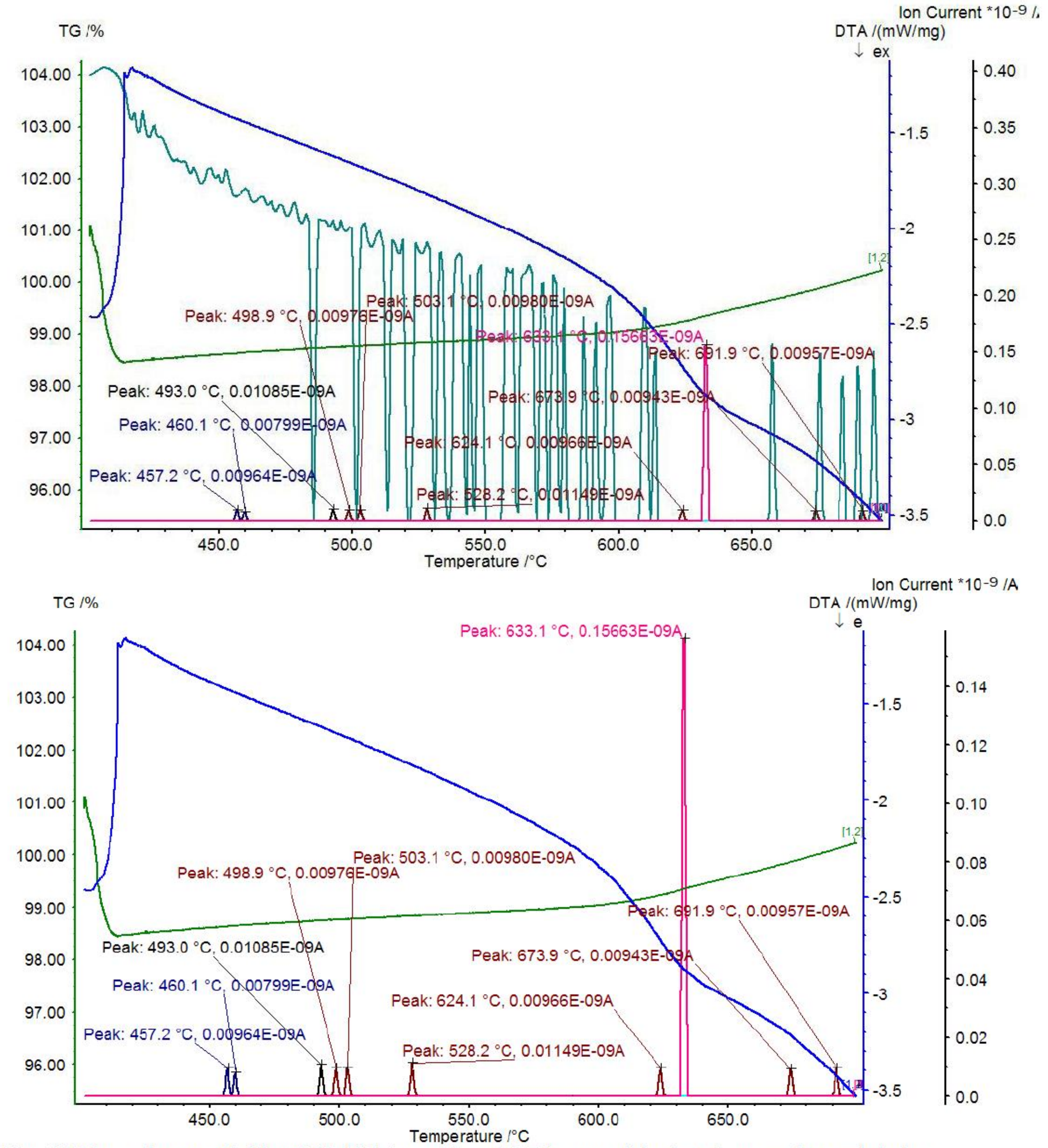

Fig 22 Mass change of Alloy 625+KCl (green) and DTA-curve (blue) and gases formed during burning He (brown, 5 amu), C (black, 12 amu), O, OH (grey, 17 amu), ?? (dark blue, 19 amu), Al (pink, 26 amu).